Exchange bias and enhancement of the Néel temperature in thin NiF$_2$ films

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Epitaxial thin (110) films of the weak ferromagnet NiF$_2$ were deposited on single-crystal MgF$_2$ (110) substrates via molecular-beam epitaxy. Subsequently polycrystalline Co was grown on the NiF$_2$ film. The antiferromagnetic ordering of the NiF$_2$ was monitored as a function of temperature via neutron diffraction and the exchange bias $H_E$ of the Co layers was measured via standard magnetometry measurements. Because in NiF$_2$ the spins lie in the (001) plane, the maximum $H_E$ is observed after cooling the sample with a cooling field in the film plane perpendicular to the [001] direction of the NiF$_2$. In 60 nm, 49 nm, and 38 nm thick NiF$_2$ samples, the Néel temperature is $T_N = 81$ K, which is significantly larger than the bulk value of $T_N = 73.2$ K. This enhancement also occurs in films without Co overlayers and thus is not due to a proximity effect. For the 38 nm sample with a Co overlayer cooled in a 50 kOe field, $H_E > 0$ and vanishes at a blocking temperature ($T_B$) which coincides with the $T_N$ of the films. When the sample is cooled in 2.0 kOe, $H_E < 0$, disappearing at $T = 55$ K, reappearing at $T = 65$ K, and finally disappearing once again at $T = 81$ K. For the 12 nm thick NiF$_2$ sample, $T_B < T_N$. Strain-induced enhancement of ferromagnetic exchange interactions between the nearest-neighbor Ni$^{2+}$ ions along the $c$ axis may be responsible for the $T_N$ enhancement. These results also demonstrate that in general, a diminished $T_B$ is not necessarily due to a lower $T_N$.

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I. INTRODUCTION

Exchange bias ($H_E$) refers to the shift of the magnetic hysteresis loop of a ferromagnet (F) away from $H=0$ when the F is coupled to an antiferromagnet (AF) or a ferrimagnet. It was originally discovered in Co particles whose surface was oxidized to form CoO. This effect has been observed in a large number of systems, including ferrimagnetic/ferrimagnetic bilayers. $H_E$ vanishes above a temperature conventionally denoted as the blocking temperature $T_B$. Bilayer systems in which the AF is below a critical thickness $T_C$, which is system dependent, generally have a much lower $T_B$ compared to the Néel ordering temperature $T_N$ of the bulk AF. This reduction of $T_B$ could be due to the decrease of $T_N$ because of finite size or strain effects, but it is often difficult to unambiguously distinguish between $T_B$ and $T_N$. By performing neutron diffraction on single crystalline Fe$_2$O$_3$/CoO multilayers, it was recently shown that the $T_N$ of CoO layers increases when the thickness of CoO is less than 5 nm, whereas $T_B$ decreases in that thickness regime. This increase in $T_N$ was interpreted to arise from the proximity of the CoO layers to the ferrimagnetic Fe$_2$O$_3$ layers, which have a much higher-ordering temperature than CoO (for bulk Fe$_2$O$_3$, $T_N = 858$ K, and for bulk CoO $T_N = 291$ K). It was also recently reported that the FeF$_2$ thin film $T_N$ can be enhanced to $T_N = 82$ K (bulk $T_N = 78.4$ K) when FeF$_2$/ZnF$_2$ multilayers are grown on MgO (100) substrates with FeF$_2$ layer thicknesses between 10 and 15 monolayers. This enhancement was attributed to the strain in FeF$_2$ due to the small lattice mismatch between these two materials.

In this paper we report on the epitaxial growth and exchange bias of the weak ferromagnet NiF$_2$. We find several interesting new phenomena, including: (1) a significant increase in $T_N$ with respect to bulk, possibly due to strain; (2) a significant exchange bias in NiF$_2$ films with Co overlayers; (3) a reentrant exchange bias behavior for intermediate (38 nm) NiF$_2$ thin-film thicknesses; and (4) a significant difference in the $T_N$ and $T_B$ for thin NiF$_2$ samples (12 nm). These results are discussed in terms of the known magnetic properties of NiF$_2$.

The properties of NiF$_2$ in bulk form can be summarized as follows. NiF$_2$ shares the rutile crystal structure with MgF$_2$, FeF$_2$, MnF$_2$, CoF$_2$, and ZnF$_2$, having lattice constants $a=b=0.4651$ nm and $c=0.3084$ nm at room temperature. For NiF$_2$ the magnetic Hamiltonian is given by

$$
\mathcal{H} = -\sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j + A \sum_i S_{iz}^2 + E \left( \sum_i (S_{ix}^2 - S_{iy}^2) - \sum_j (S_{jx}^2 - S_{jy}^2) \right),
$$

where $J_{ij}$ are magnetic exchange interactions between Ni$^{2+}$ ions, $A$ is a single-ion magnetic anisotropy, $E$ is an additional anisotropy term arising from spin-orbit coupling in the Ni$^{2+}$ ions, and the $x'$ and $y'$ axes are at 45° relative to the crystalline $a$ and $b$ axes. Also in the third term, the sums over spins $i$ and $j$ refer to spins on opposite sublattices. Because the single-ion anisotropy term $A$ is positive, at low tempera-
The canting angle is small, approximately 0.43°. This results in a small spontaneous magnetic moment, and hence NiF$_2$ is a weak ferromagnet. Single-crystal samples in principle can be made into a single magnetic domain by applying a large field along the [100] or [010] direction below $T_N$. The value of $T_N$=73.2 K has been verified on bulk single crystals via heat capacity, magnetization, and thermal expansion measurements. The low-temperature magnetic structure and the dominant exchange interactions are shown in Fig. 1.

The exchange constants have been determined from inelastic neutron scattering (ferromagnetic coupling between ions along the $c$ axis, nearest neighbors), $J_z$=−13.87 cm$^{-1}$ (antiferromagnetic coupling between nearest corner to body center ions, next-nearest neighbors), $J_3$=−0.79 cm$^{-1}$ (antiferromagnetic coupling between ions along the $a$ or $b$ axis, next-nearest-nearest neighbors). Note that $J_2$≈$J_1, J_3$, and thus dominates the exchange interactions. Spins in (110) planes are almost compensated, except for the small spontaneous canting, since the magnetic moments of the Ni$^{2+}$ ions on the vertices of the body-centered tetragonal (bct) lattice tend to point opposite to those at the center of the unit cell.

The exchange bias was measured in a superconducting quantum interference device (SQUID) magnetometer after field cooling the sample from $T$=100 K to $T=5$ K. Both the cooling field $H_{CF}$ and the measuring field $H$ were applied parallel to the NiF$_2$ [110] direction, that is, in the plane of the sample and perpendicular to the $c$ axis. No exchange bias was observed if $H_{CF}$ was applied parallel to the $c$ axis. This may occur because the moments in the F and AF layers are perpendicular to each other during cooling in this situation, so that the net interface interaction between the antiferromagnet and the ferromagnet is $J_1 \vec{S}_{F} \cdot \vec{S}_{AF}$=0, where $J_1$ is an effective interface exchange interaction and $\vec{S}_{F}$ and $\vec{S}_{AF}$ are the spins in the F and AF layers, respectively.

Additonal measurements were carried out using a vibrating sample magnetometer (VSM) which allowed us to cool the sample in a magnetic field and then rotate the sample at low temperatures in order to measure $M \perp H_{CF}$.

D. Magnetic neutron diffraction

Neutron-diffraction measurements were carried out at the NIST Center for Neutron Research. The BT-2 and BT-9 triple-axis spectrometers were used with a neutron wavelength of 0.235 nm. A closed cycle refrigerator was used to cool the sample to 12 K. The (001)NiF$_2$ magnetic Bragg reflection, which is sensitive to the ordering of spins in the (001) planes, was monitored as a function of temperature in order to determine $T_N$. Note that the existence of this reflection also proves that the magnetic order in the film is that of NiF$_2$. This peak is normally absent for the other antiferromagnetic rutile fluorides (FeF$_2$, MnF$_2$, and CoF$_2$) due to the

II. EXPERIMENTAL DETAILS

A. Growth

All samples were grown on commercially grown and polished (110) MgF$_2$ single-crystal substrates by molecular-beam epitaxy (MBE) at a growth rate of $\sim$0.02 nm/s, monitored by quartz-crystal monitors. The substrate was rinsed in methanol for 10 min prior to transfer to the MBE chamber with a base pressure of 1.0×10$^{-9}$ mbar. Before the deposition, the substrate was heated to 297°C for 30 min. NiF$_2$ was then deposited onto the substrate by electron-beam evaporation of compressed NiF$_2$ pellets. The growth pressure during evaporation was $\sim$5.0×10$^{-8}$ mbar. After the growth of the NiF$_2$ layer, a polycrystalline Co film, with a nominal thickness of 18 nm, was deposited at 125°C. The actual thicknesses were measured after growth via x-ray reflectivity, as discussed below. In order to prevent oxidation, all samples were capped with 5 nm MgF$_2$ deposited at room temperature.

B. Structural characterization

The surface crystal structure was analyzed in situ via reflection high-energy electron diffraction (RHEED). The crystalllography and interface structure was analyzed ex situ from x-ray diffraction and reflectivity data, obtained from a rotating anode source using Cu Kα radiation. In-plane lattice parameters were determined from Bragg reflections with a component of the x-ray momentum-transfer vector $q$ pointing in the plane of the sample. Reflectivity data were fit to a recursive optical model to determine the thickness of each layer, as well as the interface roughness between adjacent layers.

C. Magnetization measurements

The surface crystal structure was analyzed in situ via reflection high-energy electron diffraction (RHEED). The crystalllography and interface structure was analyzed ex situ from x-ray diffraction and reflectivity data, obtained from a rotating anode source using Cu Kα radiation. In-plane lattice parameters were determined from Bragg reflections with a component of the x-ray momentum-transfer vector $q$ pointing in the plane of the sample. Reflectivity data were fit to a recursive optical model to determine the thickness of each layer, as well as the interface roughness between adjacent layers.
neutron magnetic scattering selection rules for their localized spins pointing along the [001] direction.  

III. RESULTS AND DISCUSSION

A. Structure

Given that epitaxial growth of NiF₂ films has not, to the best of our knowledge, been reported previously, we present a detailed description of the structure of our films.

Figure 2 shows x-ray reflectivity scans for three NiF₂/Co bilayers. The fit parameters are summarized in Table I. The interface roughness parameters resulting from the fit are shown in Table I. For (a) and (b) the fitted intensity below the critical edge is larger than the measured data because at those angles that size of the sample was smaller than the x-ray beam footprint.

![Figure 2: Specular x-ray reflectivity intensity as a function of the x-ray wave vector q for NiF₂/Co bilayers with NiF₂ thicknesses of (a) 12 nm, (b) 38 nm, and (c) 49 nm. The dots are the acquired data and the solid lines are fits to a fully optical reflectivity model. The interface roughness parameters resulting from the fit are shown in Table I. For (a) and (b) the fitted intensity below the critical edge is larger than the measured data because at those angles that size of the sample was smaller than the x-ray beam footprint.](image)

<table>
<thead>
<tr>
<th>NiF₂ t</th>
<th>Co t</th>
<th>MgF₂</th>
<th>σ NiF₂/subst</th>
<th>σ Co/NiF₂</th>
<th>σ MgF₂/Co</th>
<th>σ air/MgF₂</th>
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</thead>
<tbody>
<tr>
<td>12.0</td>
<td>21.1</td>
<td>5.0</td>
<td>0.3</td>
<td>0.2</td>
<td>1.9</td>
<td>1.0</td>
</tr>
<tr>
<td>38.0</td>
<td>15.9</td>
<td>5.0</td>
<td>0.4</td>
<td>0.3</td>
<td>1.2</td>
<td>0.8</td>
</tr>
<tr>
<td>49.0</td>
<td>15.8</td>
<td>5.0</td>
<td>0.3</td>
<td>0.3</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

On the other hand, the Co surface is much rougher than the NiF₂ surface (see Table I), as is the case in FeF₂/Co bilayers.

Figure 3 shows the out-of-plane x-ray diffraction scan for the samples used in this study. The observed NiF₂ reflections are indicated by the dotted vertical lines. The dashed vertical line is the position of the Co fcc (111) or hcp (0001) reflection. The bottom panel is a scan of the substrate without overlayers, and the MgF₂ (110) and (220) peaks are labeled. The other peaks in the bottom panel, labeled with a (+) on the top panel, are unidentified substrate impurities.

![Figure 3: θ-2θ x-ray diffraction scans of the samples used in this study. The observed NiF₂ reflections are indicated by the dotted vertical lines. The dashed vertical line is the position of the Co fcc (111) or hcp (0001) reflection. The bottom panel is a scan of the substrate without overlayers, and the MgF₂ (110) and (220) peaks are labeled. The other peaks in the bottom panel, labeled with a (+) on the top panel, are unidentified substrate impurities.](image)
X-ray diffraction \( \phi \) scans demonstrated that the NiF\( _2 \) grows epitaxially on the MgF\( _2 \). Figures 5(a) and 5(b) show the in-plane \( \phi \) scans of the 60 nm thick single NiF\( _2 \) film and its substrate. The scans were carried out with the incident beam and the detector fixed at the NiF\( _2 \) \((332)\) and MgF\( _2 \) \((332)\) Bragg conditions while the sample was rotated about the surface normal. Combining the out-of-plane and in-plane scans, the epitaxial relationship was determined to be NiF\( _2 \) \([001] \parallel \) MgF\( _2 \) \([001] \) and NiF\( _2 \) \([110] \parallel \) MgF\( _2 \) \([110] \). This was confirmed by RHEED patterns obtained after the NiF\( _2 \) layer growth, as shown in Fig. 6. This pattern, obtained with the incident beam along the NiF\( _2 \) \([110] \) direction for the 60 nm thick sample, was only twofold symmetric as a result of the twofold symmetry of the \((110)\) surface. Furthermore, the streaky nature of the pattern qualitatively indicates that the surface is crystalline and smooth. The in-plane lattice parameters were determined from Bragg reflections with a component of \( \mathbf{q} \) being parallel and perpendicular to the in-plane \([001] \) direction. Figure 7 shows \( \theta-2\theta \) scans of the NiF\( _2 \) \((332)\) and \((420)\) Bragg reflections, as well as the fittings to Gaussian line shapes. After transforming the base vectors from bct \( a=[100] \), \( b=[010] \), and \( c=[001] \) to \( a'=[110] \), \( b'=[110] \), and

![Image](image1.png)

**FIG. 4.** Rocking curves for the (220) peaks of (a) 60 nm NiF\( _2 \) grown on MgF\( _2 \) \((110)\); (b) 68 nm FeF\( _2 \) grown on MgF\( _2 \) \((110)\); and (c) 69 nm FeF\( _2 \) grown on MgO \((100)\). All samples were grown under similar conditions. Samples grown on MgF\( _2 \) are epitaxial single crystalline while the sample grown on MgO \((100)\) is twinned with two equivalent in-plane \( c \) axes. The circles are the data and the solid curves are fits to Lorentzian line shapes. The widths of the fits are \(0.19^\circ, 0.50^\circ\), and \(1.8^\circ\), respectively.

![Image](image2.png)

**FIG. 5.** Typical \( \phi \) scans for the (a) NiF\( _2 \) \((332)\) and (b) MgF\( _2 \) \((332)\) Bragg reflections used to determine the epitaxial relationship of NiF\( _2 \) to the substrate: NiF\( _2 \) \([001] \parallel \) MgF\( _2 \) \([001] \) and NiF\( _2 \) \([110] \parallel \) MgF\( _2 \) \([110] \). Lines are guides to the eye.

![Image](image3.png)

**FIG. 6.** RHEED pattern of the 60 nm NiF\( _2 \) sample with the electron beam incident parallel to NiF\( _2 \) \([110] \) direction.

![Image](image4.png)

**FIG. 7.** \( \theta-2\theta \) scans of the \((332)\) and \((420)\) peaks of a 60 nm NiF\( _2 \) sample. The two peaks correspond to the Cu \( K_{\alpha1} \) and Cu \( K_{\alpha2} \) wavelengths. The data are the dots and the curves are fits to two Gaussians.
TABLE II. Lattice constants $d_{hkl}$ for NiF$_2$, Bulk NiF$_2$ and MgF$_2$ values obtained from this work. The 60 nm sample does not have a Co overlayer. Values in nanometers. Uncertainties for thin-film lattice parameters are ±0.0002 nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d_{110}$</th>
<th>$d_{110}$</th>
<th>$d_{001}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk MgF$_2$</td>
<td>0.3267</td>
<td>0.3267</td>
<td>0.3040</td>
</tr>
<tr>
<td>Bulk NiF$_2$</td>
<td>0.3289</td>
<td>0.3289</td>
<td>0.3084</td>
</tr>
<tr>
<td>60 nm NiF$_2$</td>
<td>0.3307</td>
<td>0.3272</td>
<td>0.3056</td>
</tr>
<tr>
<td>49 nm NiF$_2$</td>
<td>0.3304</td>
<td>0.3058</td>
<td></td>
</tr>
<tr>
<td>38 nm NiF$_2$</td>
<td>0.3304</td>
<td>0.3061</td>
<td></td>
</tr>
<tr>
<td>12 nm NiF$_2$</td>
<td>0.3302</td>
<td>0.3061</td>
<td></td>
</tr>
</tbody>
</table>

We see that the (332) and (420) reflections in the bct coordinate system become (302) and (310) reflections in the new indexing system. Because the [110] direction is the growth direction, and the $a'$ lattice parameter is known from the out-of-plane scan, $c'$ and $b'$ can be easily calculated. Results are shown in Table II, along with the lattice constant of bulk NiF$_2$ and MgF$_2$ and the [110] and [001] lattice parameters for the other samples used in this study. From the table it is clear that the NiF$_2$ contracts along [001] and [110] directions due to the smaller lattice constant of the MgF$_2$ substrate. However, along the surface normal, such restriction does not exist, leading to a lattice expansion along that direction. Although $d_{110}$ was not directly measured for the thinner films, it is safe to assume that it is similar to the 60 nm film value because of the similar $d_{001}$ values. Note that within the uncertainty of our measurements there is very little variation of the lattice parameters as a function of NiF$_2$ thickness, indicating that the strain is similar in all of our thin-film samples. The width of diffraction peaks with $q$ perpendicular to the surface and partially in the plane indicates that the out-of-plane and in-plane coherence lengths for the 60 nm film were 35.7 nm and 29.4 nm, respectively.

B. General magnetic properties of the samples

Representative magnetization hysteresis loops for the 49 nm sample are shown in Fig. 8. Figures 9–11 show how the exchange bias, coercivity ($H_C$), and neutron magnetic peak intensity depend on temperature for the 49 nm, 38 nm, and 12 nm samples, respectively. In all the magnetization measurements $H_{CF}$=2 kOe was applied parallel to the NiF$_2$ [110] direction. Note that for the two thicker samples $H_C$ has a peak that does not coincide with $T_B$, unlike what is observed in single crystal FeF$_2$/Co and twinned FeF$_2$/Fe samples, where the position of the peak coincides with $T_B$.\(^1\)\(^2\)\(^3\) The origin of this peak in FeF$_2$ has been attributed to short-range order above $T_N$, to the properties of the surface antiferromagnetic susceptibility,\(^2\)\(^3\) or to uncompensated spins due to domain formation in the antiferromagnet.\(^2\)\(^6\) A similar mechanism may be responsible for the behavior in NiF$_2$. Also note that for the 49 nm sample $H_E$>0, which also occurs for FeF$_2$ cooled in high fields.\(^2\)\(^7\) We have verified that $H_E$<0 at $T$=5 K when cooling in $H_{CF}$=1 kOe. These issues will be studied in more detail in a future publication.

C. Enhancement of the NiF$_2$ Néel temperature

Table III summarizes $T_N$ and $T_B$ for the different samples. Except for the thinnest sample, $T_B$, $T_N$=81 K, a significant

FIG. 8. Magnetization hysteresis loops for the 49 nm NiF$_2$/15.8 nm Co bilayer sample. Data obtained at $T$=90 K (○) and $T$=5 K (•), the latter after field cooling in $H_{CF}$=2 kOe. $H$ and $H_{CF}$ were applied along the NiF$_2$ [110] direction.

FIG. 9. (a) Exchange bias and coercive field of a 49 nm NiF$_2$/15.8 nm Co bilayer as a function of temperature after cooling in $H_{CF}$=2 kOe. (b) Temperature dependence of the (001) NiF$_2$ neutron magnetic peak intensity after field cooling in $H_{CF}$=550 Oe and $H_{CF}$=0. Solid lines are linear fits to the data points close to $T_N$ for $H_{CF}$=0. The intersection of the lines yields $T_N$. The dashed vertical line indicates $T_B$ and the solid vertical line indicates $T_N$. 

...
enhancement over the accepted $T_N$ of bulk NiF$_2$ (73.2 K). The value for the thinnest sample, obtained from Fig. 11, is actually a lower, conservative bound. The actual Néel temperature for this sample could be as high as 85 K, but the relatively weak signal near $T_N$ makes it impossible to obtain a better measurement. An important question is whether $T_B$ is enhanced by a larger $T_N$ of the NiF$_2$ film. If so, the question is whether it results from a proximity effect, where the Co film, due to its high Curie temperature ($T_C$ = 1388 K in bulk form), causes the NiF$_2$ to order at an unusually high temperature. As mentioned above, this has been observed experimentally in Fe$_3$O$_4$/CoO multilayers and has also been confirmed theoretically using Monte Carlo simulations. Note that the values of $T_N$ obtained from neutron data with and without field cooling for the 49 nm and 38 nm samples are almost identical, taking into account the error bars, indicating that $T_N$ does not depend on $H_{CF}$. The background of the magnetic (001) peak is due to the nuclear contribution of the MgF$_2$ substrate. The integrated intensity of (001) peak (not shown here) gives exactly the same temperature dependence as that of the peak intensity.

We also measured the magnetization along the [110] direction of a 60 nm thick single NiF$_2$ film with no Co overlayer, in addition to neutron-diffraction measurements. Figure 12(a) shows the NiF$_2$ (001) peak intensity as a function of temperature after field cooling ($H_{CF}$=550 Oe) and zero-field cooling. Note that $T_N$=81 K, as was the case for the bilayer samples shown in Figs. 9 and 10, indicating that the enhancement of $T_N$ is not due to the proximity effect. Figure 12(b) shows magnetic susceptibility $\chi$, defined as $\chi=M/H$, of this sample with a 2.3 kOe field applied along the NiF$_2$ [110] direction as a function of temperature, after cooling from $T$=100 K to $T$=5 K in $H_{CF}$=2 kOe. Because NiF$_2$ is only a weak ferromagnet, the peak in $\chi$ corresponds to $T_N$. The inset of Fig. 12(b) shows $d\chi/dT$, from which we determined that the peak of $\chi$ is at $T_N$=79.7 K. This result indeed agrees very well with the neutron-scattering result; the small disagreement may be due to different thermometry set-ups.

<table>
<thead>
<tr>
<th>NiF$_2$ thickness (nm)</th>
<th>$T_B$ (K)</th>
<th>$T_N$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>53.1±0.5</td>
<td>78(−1±7)</td>
</tr>
<tr>
<td>38</td>
<td>81.5±0.5</td>
<td>83.7±2</td>
</tr>
<tr>
<td>49</td>
<td>81.0±0.5</td>
<td>82.3±2</td>
</tr>
<tr>
<td>60</td>
<td>81.4±2</td>
<td></td>
</tr>
</tbody>
</table>
FIG. 12. (a) Temperature-dependent intensity of the (001) magnetic reflection for the 60 nm NiF$_2$ film after field cooling and zero-field cooling. Note that $T_B=81$ K. Lines are linear fits to the data close to $T_N$ for $H_{CF}=0$. (b) Magnetic susceptibility $\chi=M/H$ as a function of temperature after cooling the sample from $T=100$ K to $T=5$ K in $H_{CF}=2$ kOe. Both the cooling field and the measuring field ($H=2300$ Oe) are parallel to the NiF$_2$ [110] direction. The inset shows the first derivative of $\chi$ with respect to the temperature. $T_N=79.7$ K from the point at which $d\chi/dT=0$.

The values of $T_N$ and $T_B$ for all the samples are shown in Table III.

To interpret the enhancement of the films’ $T_N$ with respect to bulk material, we first note that bulk NiF$_2$ has lattice constants that are similar to those of the MgF$_2$ substrate. As indicated by the x-ray structural analysis above (Table II), the NiF$_2$ films grow strained in order to be lattice matched to the substrate crystal structure. This strain causes a significant orthorhombic distortion of the lattice throughout the entire thickness. It is therefore important to determine whether this distortion is responsible for the enhancement of $T_N$. Unfortunately, the dependence of $T_N$ on pressure or lattice parameters has not been studied in NiF$_2$, so it is not possible to directly compare our results with experimental data. One may assess this issue by using results from other magnetic materials. Specifically, in many antiferromagnets a change in the unit-cell volume is related to a change in effective exchange interaction by

$$\frac{d(\ln J)}{d(\ln V)} = -\gamma_m, \tag{2}$$

where $V$ is the volume of the unit cell, $d(\ln J)\propto J_s/J_o$, and $d(\ln V)\propto V_s/V_o$. Here $J_s$ and $V_s$ refer to the sample exchange and volume, respectively, and $J_o$ and $V_o$ refer to the exchange and volume of the bulk crystal. This $\gamma_m$ is an effective magnetic Gr"uneisen constant which for a wide array of magnetic materials $\gamma_m=10/3$, including FeF$_2$ (Ref. 30) and MnF$_2$.\textsuperscript{31} Assuming that NiF$_2$ obeys the 10/3 law; using the mean-field result that $T_N\propto J$ (known to be accurate for calculating changes in $T_N$) (Ref. 32); and using $V=2d_{110}d_{100}/3$, we obtain that $\Delta T_N=2.4$ K. This is smaller than our experimental value of $\approx 8$ K by a factor of 3. The lattice mismatch at low temperatures between MgF$_2$ and NiF$_2$ is smaller than at room temperature,\textsuperscript{33} so the expected change in $T_N$ discussed here is an upper bound. The large relative change of the $c$-axis lattice parameter would seem to indicate that a change in $J_1$ might be responsible for the enhanced $T_N$, but this is unlikely because $J_1$ is more than 60 times smaller in magnitude than $J_2$.

Our results therefore suggest that $\gamma_m$ is anomalous for NiF$_2$. One possibility is that the fluorine ions are displaced from their equilibrium positions, independent of the lattice expansion or contraction, which could have a significant effect on the exchange interactions. NiF$_2$ is known to have a significant magnetostrictive shift of the fluorine ions at low $T$ with respect to the value above $T_N$, unlike FeF$_2$.\textsuperscript{33,34} Further neutron and x-ray measurements are needed to determine whether this is the case.

D. Reentrant exchange bias

Figure 10 shows the exchange bias and the NiF$_2$ (001) peak intensity as a function of temperature in the 38 nm bilayer sample. For a small cooling field ($H_{CF}=2$ kOe) $H_E$ shows a reentrant behavior. In other words, it goes to zero at $T\sim 55$ K and then becomes negative before it vanishes again at $T=81$ K. On the other hand, if the cooling field is sufficiently large ($H_{CF}=50$ kOe, see Fig. 13), $H_E$ remains positive before it vanishes at the same blocking temperature, $T_B=81$ K. This behavior is similar to the change in sign of $H_E$ as a function of $T$ in Fe$_{23}$Zn$_{1-x}$F$_2$/Co bilayers, with $x\sim 0.80$, where $H_E$ can be zero at an intermediate temperature for moderate cooling fields.\textsuperscript{35} For the case of the NiF$_2$, when $H_E$ goes to zero as the sample is warmed, instead of becoming positive at higher temperatures, it becomes negative once again. It is unclear whether the change in sign of $H_E$ in Fe$_{23}$Zn$_{1-x}$F$_2$ and the reentrant effect in NiF$_2$ are related. However, it is possible that for NiF$_2$ this is a result of a reorientation of the antiferromagnetic domains from the (100) plane to the (010) plane or vice versa. A similar reentrant effect, although less marked, has been observed in FePt$_3$/Fe
and its origin is believed to result from a spin reorientation in the antiferromagnet, similar to the one discussed here, that has been observed via neutron scattering. Further neutron-diffraction measurements of the magnetic (100) peak are planned to determine whether this is true. Unfortunately a substrate contamination peak precluded us from performing these measurements with high accuracy in these samples, so better substrates will be needed.

E. Reduction of $T_B$ in thin NiF$_2$

Figure 11(a) shows $H_E$ as a function of temperature for a 12 nm thick NiF$_2$ sample. In this case $T_B$ is reduced to $T = 53$ K. However, the integrated NiF$_2$ (001) peak intensity, as shown in Fig. 11(b), indicates that $T_N \approx 78$ K, with an uncertainty of approximately $-1 \pm 7$ K. Hence, $T_N$ is certainly above 70 K, and is possible as high as 85 K. Note that all the data in Fig. 11(b) are plotted after subtracting the nuclear MgF$_2$ (001) peak measured at $T = 90$ K. This shows that the reduced $T_B$ is not due to a diminished $T_N$, but is probably due to the AF domains in the NiF$_2$ becoming unpinned above $T = 53$ K. This is consistent with measurements in single crystals that suggest that the magnetization in the $a$-$b$ plane becomes isotropic close to $T_N$.\textsuperscript{15} It is not surprising that for small NiF$_2$ thicknesses this effect would be magnified because the total magnetic anisotropy energy is proportional to the volume, and therefore, the thickness of the film. It is also interesting to note that the temperature at which $H_E$ goes to zero for the first time (53 K) in the 38 nm sample coincides with $T_B$ for the 12 nm sample. Further measurements are required to determine whether this is a coincidence, or if $T = 50$ K is the temperature where the magnetic in-plane anisotropy of the NiF$_2$ ‘softens’ up. In any case, this is a clear experimental demonstration that, in general, a low $T_B$ is not necessarily due to a lower $T_N$, due to finite-size effects, for example, but could be due to other factors, such as a smaller effective anisotropy energy that can no longer withstand its magnetic structure at higher temperatures.

IV. CONCLUSIONS

In summary, (110) NiF$_2$ was epitaxially grown on (110) MgF$_2$ substrates via MBE. In thicker NiF$_2$, $T_N$ and $T_B$ are significantly larger than the bulk value. This enhancement of $T_N$ is likely to be a result of the strain in NiF$_2$ due to a small lattice mismatch between the NiF$_2$ films and the MgF$_2$ substrates. In order to calculate the enhancement of $T_N$ due to the strain in NiF$_2$, the dependence of $J_2$ not only on the lattice parameters, but possibly also on the position of the fluorine ions is needed. A reentrant exchange bias behavior was also observed for the 38 nm sample. For the thinnest, 12 nm sample, $T_B \ll T_N$, indicating that the antiferromagnet’s anisotropy is not enough to maintain the exchange bias at higher temperatures below $T_N$, even though long-range order in NiF$_2$ is maintained.

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