

Correlation between microstructural and magnetic properties in Fe/KCoF₃ bilayers

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Molecular beam epitaxy was used to grow a ferromagnet/antiferromagnet (Fe/KCoF₃) system. A series of structural, surface, and magnetic characterization techniques were used to understand the correlation between microstructural and magnetic properties in this exchange bias system. Depending on deposition conditions, the fluoride grew either in a single crystal or a polycrystalline form, which was initially confirmed by reflection high energy electron diffraction patterns and x-ray studies. The crystalline form of the KCoF₃ significantly affected the magnetic properties, in particular the exchange bias and the magnetocrystalline anisotropy of the Fe layer. Transmission electron microscopy (TEM) studies were carried out to shed more light on the microstructure of the fluoride and on the interface between Fe and KCoF₃ layers. Single crystal KCoF₃ layers grown at elevated temperature on (001) Fe template have a (001) orientation. On the other hand, the cross-sectional TEM images of the polycrystalline fluoride deposited at room temperature show columnar structure of the grains with a column diameter of about 10 nm. In addition, planar defects were observed in the Fe layer due to the slight mismatch between Fe and KCoF₃ lattices. These defects and grain boundaries in the antiferromagnet are responsible for considerable modification of magnetic properties of the structures with polycrystalline fluoride compared to those with the single crystal KCoF₃. Magnetic anisotropy and the exchange bias were measured using ferromagnetic resonance and superconducting quantum interference device magnetometry, respectively. The exchange bias and blocking temperature in the samples with polycrystalline fluoride were significantly reduced, however, the low-temperature fourfold anisotropy was enhanced by a factor of 3 for the samples with 1-nm-thick Fe and polycrystalline fluoride compared to the samples with the same thickness of Fe but single crystal fluoride. © 2003 American Vacuum Society.

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I. INTRODUCTION

Studies of ultrathin magnetic films have attracted considerable attention¹ in the last two decades. Progress in ultrahigh vacuum technology and especially the use of molecular beam epitaxy (MBE) has made possible the creation of ultrathin structures with interfaces that are sharp on the atomic scale. This development has brought exciting ways of engineering new magnetic materials. Three significant experimental discoveries, giant magnetoresistance,² exchange coupling between ferromagnetic layers,³ and giant magnetic anisotropies,⁴ have sparked tremendous interest among physicists in this new class of artificially structured magnetic materials. The giant magnetic anisotropy in ultrathin magnetic layers is peculiar since it can be caused by many dif-

ferent factors, for example, the change of crystal symmetry of the magnetic layer at the interface, the stresses due to lattice mismatch at the interface and different thermal expansion coefficients of two adhering layers. The effect of stresses can be greatly enhanced in the case of magnetostrictive materials. On the other hand, the exchange interaction averages out the magnetic anisotropies of the individual atoms across the film thickness for systems thinner than an exchange length,¹ thus allowing us to engineer their magnetic properties.

One special case occurs as a result of the exchange interactions between ferromagnetic and antiferromagnetic materials where a unidirectional anisotropy can be induced. This occurs when the structure is cooled in the presence of a magnetic field below the Néel temperature of the antiferromagnet.⁵⁻⁷ In magnetic measurements, this unidirec-

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tional anisotropy causes a shift of the magnetization hysteresis loop, called exchange bias. We studied both the structure and magnetic properties of the exchange biased system consisting of a thin ferromagnetic single crystal Fe (001) film and an antiferromagnetic fluoride— KCoF_3 . The fluoride is a model Heisenberg antiferromagnet with Néel temperature of 114 K.^{8,9} It is also highly magnetostrictive ($\lambda = 2 \times 10^{-3}$). In the bulk form, the KCoF_3 crystallizes as a perovskite, with a cubic lattice constant $a = 0.408$ nm.¹⁰ This system has a type-G antiferromagnetic order, where one Co cation has antiferromagnetic coupling with all the nearest-neighbor Co cations. The magnetic unit cell has four formula units per cell. KCoF_3 exhibits a small tetragonal distortion ($c/a = 0.998$ at 78 K) accompanying the antiferromagnetic long-range order. The equilibrium direction of the spins is parallel to the tetragonal axis c in the bulk form.^{11,12} An important feature is that KCoF_3 films can be grown with the [001] axis directed normal to the interface. If these mentioned above bulk properties remain the same in our thin films, one would expect a compensated interface for a single crystal structure with a (001) surface. Due to the good lattice match between Fe and KCoF_3 , the strains should be small at the interface and epitaxial Fe/ KCoF_3 structures can be grown. The aim of the work is to correlate the structural properties with magnetic properties of this exchange biased system.

In this article, we present a comprehensive study, concentrating on the structural, surface, and magnetic properties of Fe/ KCoF_3 structures, investigated by a series of complementary methods. We first briefly describe the experimental techniques, sample preparation, and the conditions at which the measurements were carried out. Our main structural result is that there is a significantly larger number of defects at the ferromagnet/antiferromagnet interface for samples with a polycrystalline fluoride compared to samples with single crystal fluoride. The crystallographic structure of the antiferromagnet significantly affects the magnetic properties of the Fe films. Samples with polycrystalline fluoride show a significant increase of magnetocrystalline anisotropy in Fe and much lower exchange bias when compared with samples with single crystal fluoride.

II. EXPERIMENT ASPECTS

We used a molecular beam epitaxy system¹³ to prepare our samples. All elements were evaporated using the Knudsen cells, with the exception of the fluoride, which was evaporated with an electron beam. The thickness of the individual layers was determined using a quartz crystal monitor. Reflection high energy electron diffraction (RHEED) was utilized to monitor *in situ* the crystallographic structure. The chemistry of the surfaces was examined using Auger electron spectroscopy.

For the x-ray diffraction experiments, we employed a Philips-XPert diffractometer with Cu $K\alpha$ radiation, an Eulerian cradle and a thin-film attachment. We performed both low- and wide-angle measurements after careful sample adjustments using reflectometry methods. To investigate the grain morphology and layer structure on cross sections, we

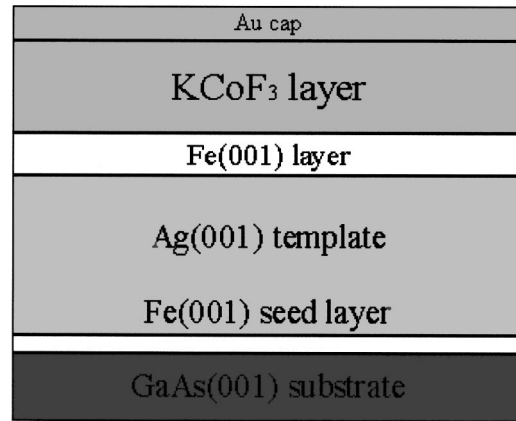


FIG. 1. Schematic diagram of the Fe/ KCoF_3 structure.

used analytical transmission electron microscopy (TEM). We prepared our samples by the conventional face-to-face technique with sticking, grinding, dimpling, and ion milling, as well as by the focused ion beam technique. The transmission electron microscopy studies were carried out using the JEOL (model 2010) Supertwin TEM. The x-ray photoelectron spectroscopy (XPS) measurements were performed with a Physical Electronics PHI 5700/660 spectrometer, using monochromatized Al $K\alpha$ radiation (1486.6 eV) and energy resolution of ~ 0.35 eV.

To determine the magnetic properties, we carried out measurements using two ferromagnetic resonance (FMR) setups operating at 10 and 24 GHz with a cylindrical cavity (TE_{011} -mode).¹⁴ The 24 GHz FMR system operated in the temperature range between 24 and 360 K. We evaluated magnetocrystalline, uniaxial and unidirectional anisotropy components from the angular dependence of the resonant fields at different temperatures. Precise measurements of the shift of magnetization hysteresis loops were determined in the temperature range from 5 to 300 K using a sensitive superconducting quantum interference device (SQUID) magnetometer (Quantum Design). For the SQUID measurements, the samples were cooled below the Néel temperature of 114 K in the presence of a positive magnetic field of 10 kOe, while the FMR field cooled experiments used a field of 6 kOe.

Figure 1 shows a schematic diagram of our structures. We prepared Ga terminated GaAs (001) wafers by annealing at 540 °C and Ar sputtering. First we deposited a few monolayers thick Fe seed layer (typically 0.75 nm thick) and an 80-nm-thick silver template. We annealed these structures at 250 °C for several hours. We then grew single crystal Fe (001) layers with thicknesses from 1 to 3 nm on the Ag template and used the electron beam evaporator to deposit a 30-nm-thick film of KCoF_3 . The deposition conditions affected the structure of the fluoride. For the deposition at room temperature with high deposition rates (above 0.5 nm/s), the fluoride films were polycrystalline as indicated by the RHEED images [see Fig. 2(a)]. Typical for the polycrystalline structures, rings were clearly visible. By depositing fluoride at an elevated temperature of 150 °C and at low deposi-

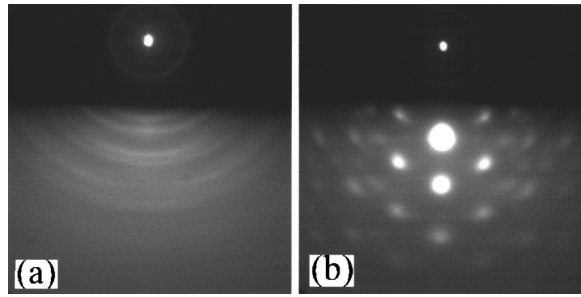


FIG. 2. RHEED images of the sample with (a) polycrystalline fluoride, (b) single crystal fluoride.

tion rates, below 0.1 nm/s, it was possible to achieve a dramatic improvement in the quality of the film. Figure 2(b) shows the single crystal structure in the film grown on the top of the Fe. The samples were covered with a thin, 3-nm-thick layer of Au. We also prepared a series of KCoF_3 samples grown directly on GaAs substrates for the x-ray and XPS studies. These films, grown at elevated temperature ($\sim 150^\circ\text{C}$), were 100 nm thick and the RHEED images suggested that they are single crystalline. We note that growing the fluoride on top of the Fe results in a smoother interface compared to growing Fe on top of the fluoride.

III. STRUCTURAL AND SURFACE CHARACTERIZATION

While the growth of Fe layers on Ag using GaAs substrates has been studied very extensively,^{15,16,17} the deposition of the KCoF_3 layers has been initiated in our laboratory. The stoichiometry of such fluoride films is an important issue. To resolve this issue we have studied the single crystal KCoF_3 film (as indicated by the RHEED images) deposited directly on the GaAs substrates using x-ray diffraction and XPS. Figure 3 shows the diffraction pattern of the KCoF_3 film measured with symmetrical beam (Bragg–Brentano geometry, solid line) and, for comparison, a measurement of the substrate itself (dotted line). The pattern clearly shows the $\{h00\}$ reflections of the GaAs substrate and the $\{100\}$, $\{200\}$, and $\{400\}$ reflections of the epitaxially (100) grown fluoride film,¹⁸ as well as additional reflections from the sub-

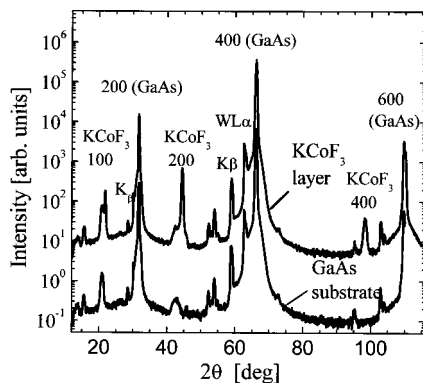


FIG. 3. $\theta-2\theta$ scans of the KCoF_3 film (solid line) and of the GaAs substrate (dotted line).

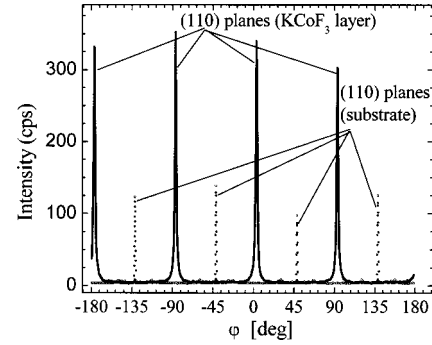


FIG. 4. KCoF_3 film ϕ scans (in-plane rotation). The unit cells of film and substrate are rotated 45° against each other.

strate. Due to the peak widths, it is reasonable to assume that the KCoF_3 grains are grown through the complete film in the vertical direction (100 nm). No signs of other texture components are visible from the KCoF_3 diffraction pattern in Fig. 3.

Figure 4 shows the measurement of the in-plane orientation distribution for the KCoF_3 sample. The measurement of the $\{110\}$ reflections of the film at $\psi=45^\circ$ shows a fourfold pattern, thus indicating the presence of only one in-plane texture component of the film ($\{100\}$ planes parallel to the sample side faces). Additional scans at the Bragg angles of other reflections confirmed that no other texture components are present. However, peaks of the $\{110\}$ substrate planes (Fig. 4, dotted line) indicate that the in-plane orientation of the film is rotated by 45° with respect to the substrate, which was expected from the lattice mismatch between GaAs (as well as Fe) and KCoF_3 .

We note that the x-ray measurements were performed on 100-nm-thick fluoride, while most other measurements were made on samples with thinner (30 nm) fluoride films. The thickness of the fluoride film was increased for the x-ray measurements to enhance scattering intensity. The main conclusion from the x-ray studies is that the fluoride film has the correct lattice constant and can be grown in single crystal form. This is consistent with all of our other measurements on thinner fluoride films as we shall demonstrate.

The XPS survey spectrum of the as-grown layer shows the lines from the components of KCoF_3 and a relatively low amount of carbon and oxygen (see Fig. 5). Low intensity lines from As and Ga can also be detected. The escape depth of photoelectrons at the XPS regime is about 1–2 nm, so the presence of the elements from the substrate indicates some minor introduction of As and Ga to the structure of the layer. The quantity of As (less than 1 at. %) is a few times larger than the Ga. Table I shows the surface composition of the layer. The composition of the sample, when neglecting the surface contaminants and elements from the substrate, agrees well with the nominal atomic concentrations. A slight deficiency of fluorine may be related to the top atomic layer terminating the single crystalline KCoF_3 . It contributes considerably to the spectrum and usually has a slightly different atomic composition.

Both techniques, x-ray and XPS, confirmed the RHEED

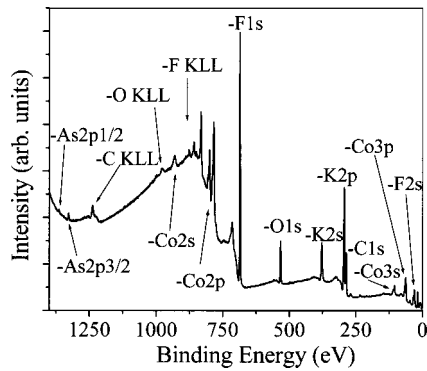


FIG. 5. XPS survey scan.

observations. During the evaporation of the fluoride a stoichiometric film is deposited, and the polycrystalline or single crystal form of the layer is properly identified by RHEED images. We stress this point since obtaining RHEED images of an ionic film is not easy. The film becomes charged and as a result the RHEED features are smeared. Also the RHEED's 15 keV beam of electrons starts to evaporate the fluoride within a second, leaving permanent marks on the film.

To image the interface of the Fe/KCoF₃ structures, we used high resolution TEM. Figures 6(a) and 6(b) show two cases—structures with polycrystalline and single crystalline KCoF₃. For the polycrystalline fluoride, the films grew in the form of columns with an average diameter of 10 nm. The crystallographic orientation of the grains differs from grain to grain and the defects originate at the Fe/KCoF₃ interface. The single crystalline structures, on the other hand, show smooth interfaces with the arrangement of atoms in the [001] direction normal to the substrates. The average terrace size at Fe/KCoF₃ interface exceeds 10 nm. For both types of structures, the arrangement of atoms in Ag, Fe, and KCoF₃ layers is clearly visible on the cross-sectional high-resolution transmission electron microscope images.

IV. MAGNETIC RESULTS AND DISCUSSION

Before we present the results of the magnetic measurements we would like to comment on the importance of the quality and type of the Fe/KCoF₃ interface. The crystalline form of the antiferromagnetic fluoride determines the magnetic properties of the interfacial Fe atoms as it will be apparent from magnetic measurements. In the case of the single crystal fluoride the spins at the ferromagnet/antiferromagnet interface are expected to be compensated. However, for the

TABLE I. Atomic concentration (%) including all elements, calculated from the XPS survey spectrum (first row). Atomic concentration of the fluoride components, calculated from the high resolution spectra (second row).

C (1s)	O (1s)	F (1s)	K (2p)	Co (2p)	Ga (2p3)	As (2p3)
18.5	11.1	38.6	15.3	15.8	0.08	0.63
		54.3	23.8	21.9		

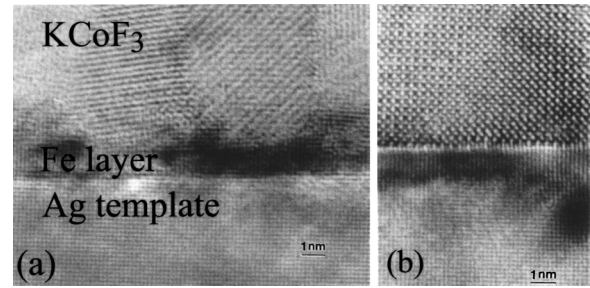


FIG. 6. TEM cross-sectional images of the MBE grown structures of Fe/KCoF₃ on a silver template. (a) Structure with the polycrystalline fluoride. (b) Epitaxial growth of the fluoride.

columnar structure of the polycrystalline fluoride with different crystallographic orientation of the columns, the spin structure at the interface will be quite different because a substantial part of antiferromagnet spins will not match the (001) orientation of the Fe. Consequently, there could be a large fraction of uncompensated spins at this interface. In addition, there are networks of defects at the Fe/KCoF₃ interface.

We note that exchange biasing has been studied previously in other fluorides. In most cases, the Fe/FeF₂ system is a good example;¹⁹ the antiferromagnetic fluoride has strong uniaxial anisotropy. In contrast, our studies focus on an antiferromagnet with a small uniaxial anisotropy but with a large exchange coupling within the antiferromagnet. This allows us to explore different features in the magnetic properties of the coupled system.

Our SQUID measurements show that the magnitude of the exchange bias at low temperatures is larger for the samples with the single crystal fluoride (see in Fig. 7). The exchange bias decreases with increasing temperature and vanishes at the blocking temperature, which is close to the Néel temperature. In contrast, the exchange bias in the samples with polycrystalline fluoride is smaller and decays much faster with the temperature. In addition, the blocking temperature is much lower than the Néel temperature. Our FMR measurements of the unidirectional anisotropy were consistent with the SQUID results of exchange bias. This result is surprising since the structures with the single crystal

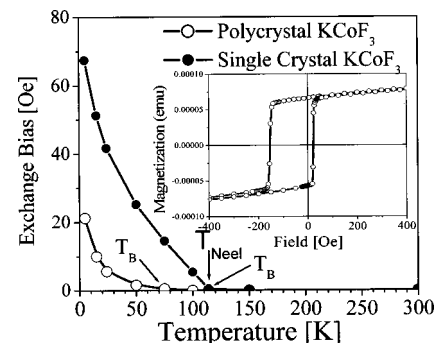


FIG. 7. Temperature dependencies of the exchange bias for the samples with 1.3 nm Fe film and single crystal or polycrystalline fluoride. The inset shows an example of the hysteresis loop illustrating the exchange bias effect.

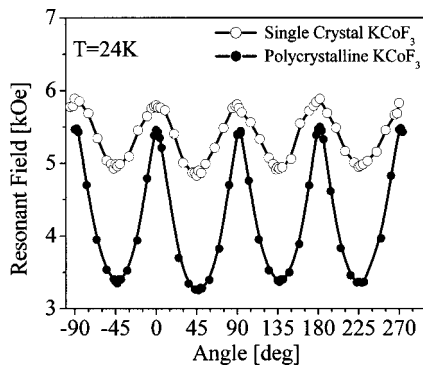


FIG. 8. Angular dependence of the resonance field in FMR at $T=24$ K for the systems with 1.05-nm-thick Fe and single crystal or polycrystalline fluorides.

fluoride are expected to have magnetically compensated surfaces, and therefore should have a smaller exchange bias.⁵

We also observed a dramatic effect of the fluoride structure on the magnetocrystalline anisotropy of the Fe layer. The fourfold anisotropy of thin Fe films was similar for the samples with polycrystalline and single crystal KCoF_3 at room temperature. However, there was a significant difference between these two types of samples at the temperatures lower than the Néel temperature. An example of this can be seen in the angular dependence of the resonant fields measured by FMR at 24 K for two samples with the same Fe thickness but different crystalline structure of the fluoride, as shown in Fig. 8. The anisotropy in the samples with single crystal KCoF_3 is comparable to that of a single Fe layer. However, in the system with the polycrystalline fluoride, the magnitude of the fourfold anisotropy is substantially larger. This enhancement of the magnetocrystalline anisotropy is the most pronounced in the thinnest samples and it decreases with increasing Fe film thickness, evidence for the interfacial origin of this effect. The source of the anisotropy enhancement may be related to the increased number of structural defects in the fluoride, which generate local stresses at the interface. This can be an especially important factor in the case of KCoF_3 , which is an antiferromagnet with giant magnetostriction. In contrast, samples with the single crystal fluoride are expected to have spin compensation at the interface and have an excellent lattice match between the Fe and the fluoride structure (mismatch is only 0.25%). The small number of dislocations observed by the TEM cannot significantly change the magnetic properties of the structure as a whole.

In conclusion, the differences in the crystallographic and magnetic structures at the ferromagnetic/antiferromagnetic

interface for the samples with single crystal or polycrystalline fluorides have an important effect on the exchange interactions and the exchange bias in this system. It is not known whether the structural changes (single crystal versus polycrystalline) or properties of the interface (interdiffusion, roughness, etc.) cause the measured changes, but the changes in the magnetic properties do correlate strongly with changes in the structure of the fluoride. The exchange bias is significantly larger for the Fe/ KCoF_3 structures with the single crystal fluoride. In contrast, the fourfold anisotropy of the Fe film is significantly increased for structures with the polycrystalline fluoride.

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