Enhanced moments in bcc $\text{Co}_{1-x}\text{Mn}_x$ on $\text{MgO}(001)$

R. J. Snow^a, H. Bhatkar^a, A. T. N'Diaye^b, E. Arenholz^b, and Y.U. Idzerda^{a}*

^aDepartment of Physics; Montana State University; Bozeman, MT 59715, United States

^bAdvanced Light Source; Lawrence Berkeley Nat. Labs; Berkeley, CA 94720, United States

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*Corresponding author: Idzerda@montana.edu

ABSTRACT

A 40% enhancement of the Co magnetic moment has been found for thin films of bcc $\text{Co}_{1-x}\text{Mn}_x$ grown by molecular beam epitaxy on a 2 nm bcc Fe buffer layer on $\text{MgO}(001)$. Although the bcc phase cannot be stabilized in the bulk, we confirm that it is stable as an epitaxial film in the composition range $x = 0-0.7$. Using X-ray absorption spectroscopy and X-ray magnetic circular dichroism, we show that the Co moment is a maximum of $2.38 \mu_B$ at $x = 0.24$, while the net Mn moment remains roughly constant until $x = 0.24$, then drops steadily. Mn is found to align parallel with Co for all ferromagnetic concentrations, up to $x = 0.7$, where the total moment of the film abruptly collapses to zero, most likely due to the onset of the observed structural instability.

1. Introduction

The Slater-Pauling curve, and in particular the generalized Slater-Pauling curve, can serve as a guide to understanding the composition dependent magnetic moment variation of a large number of binary alloys. In a recent paper [2], thin films of $\text{Fe}_{1-x}\text{Mn}_x$ grown epitaxially on $\text{MgO}(001)$ were found partly to follow and then to diverge precipitously from the expected generalized Slater-Pauling curve. Additionally, a very small x-ray magnetic circular dichroism (XMCD) signature of the ferromagnetic moment was found for the Mn atoms for all concentrations, in spite of a robust ferromagnetic signal for the Fe moment. It was thought that the precipitous drop in the magnetic moments was due to a non-collinear moment orientation of the Mn moments. To contrast $\text{Fe}_{1-x}\text{Mn}_x$ on MgO with a similar system and to further investigate the elemental moment variation near the peak of the Slater-Pauling curve, we have grown a large variety of compositionally distinct thin films of $\text{Co}_{1-x}\text{Mn}_x$ on $\text{MgO}(001)$ substrates.

The interesting phase diagram of bulk $\text{Co}_{1-x}\text{Mn}_x$ includes a martensitic transition from hcp to fcc and several magnetic phases including ferromagnetism, paramagnetism, super-paramagnetism, super-antiferromagnetism, and antiferromagnetism [3, 4], but does not show a stable bcc phase. Co and Mn magnetic moments in the fcc structure have been investigated by neutron diffraction and by NMR with some disagreement on the size and alignment of the Mn moment, with values at low concentration ranging from $-1.0 \mu_B$ to $+3 \mu_B$ [5-10] where the negative sign implies an anti-aligned Mn moment. Several mechanisms have been proposed to explain a small average moment of Mn, including the presence of both aligned and anti-aligned Mn moments [8], but a static configuration is argued against by Cable in favor of dynamic fluctuations [6, 11]. For all concentrations in the bulk fcc and hcp systems, Co and Mn moments and the average magnetization are reduced relative to that of pure Co, or in the case of Mn, relative to Mn moments in low concentration $\text{Co}_{1-x}\text{Mn}_x$.

Epitaxial thin films of $\text{Co}_{1-x}\text{Mn}_x$ have displayed small ferromagnetism enhancements relative to bulk alloys [5, 9, 12-17]. In fcc growths on Si [14], for example, the ferromagnetism was slightly enhanced for low concentrations and stabilized up to concentrations around $x = 0.70$ (70% Mn atomic concentration), while bulk alloys are ferromagnetic only up to around $x = 0.30$. The improved magnetization for fcc alloys, however, did not exceed that of pure Co. In bcc growths on GaAs, some ferromagnetic enhancements were found [13, 15, 16], and there was some indication that the magnetization was enhanced relative to pure Co [15]. Still, a direct measurement of magnetic moments and alignment in this structure, to our knowledge, has not been published.

Thin films of $\text{Co}_{1-x}\text{Mn}_x$ have been grown by MBE and monitored by RHEED, with epitaxial bcc growth accomplished by use of a crystalline bcc Fe buffer layer which prevents the oxidation of Co. The Co moment increase and the Mn parallel alignment in this system produce a significant enhancement in the average magnetization relative to that of pure Co. Using a low-concentration Mn moment of $3.0 \mu_B$ [15] the average magnetization lies on the Slater-Pauling (SP) curve for concentrations up to about $x = 0.25$, where it reaches a maximum moment of $2.38 \mu_B/\text{atom}$. This peak is shifted and the slope is steeper on the high-Mn concentration side of the peak relative to the standard SP curve. This is in stark contrast to the bulk fcc CoMn and hcp CoCr behavior which shows only a rapid total moment reduction with Mn concentration.

Due to the relatively high magnetoresistance (410% at RT) of Co/MgO/Co magnetic tunnel junctions [18], the enhanced magnetic properties of $\text{Co}_{1-x}\text{Mn}_x$ make it an interesting candidate for magnetic tunnel junctions and other magnetic device applications.

2. Experiment and Results

2.1 Growth

Molecular beam epitaxy (MBE) was used to produce single-crystal epitaxial ultrathin films. A polished MgO(001) substrate was selected for comparison with previous work and for the expected bcc structure of epitaxial metallic growths. The experimental lattice constant of MgO is 4.21 Å with a O-O distance at the surface of the MgO(001) crystal of 2.98 Å [19] that is 4% larger than bcc Fe (2.87 Å) and 5% larger than bcc Co (2.83 Å). The compositional lattice parameters for the bulk bcc $\text{Co}_{1-x}\text{Mn}_x$ alloy are estimated to be 2.85, 2.86, 2.88, and 2.89 Å at $x = 0.25, 0.50, 0.75$, and 1.00, respectively [15]. This represents a composition dependent lattice mismatch of 3% at the pure Mn end of the compositional range and 5% at the pure Co end. This suggests that growth on MgO(001) of the entire CoMn alloy compositional range should be possible since both bcc Fe and bcc Co can be grown on MgO.

Prior to MBE growth, substrates were sonicated in methanol for five minutes, sonicated in acetone for five minutes, dried under flowing N_2 air, mounted on a molybdenum holder with indium solder, loaded into the MBE load-lock, and then annealed under high vacuum to 800°C. Due to the hygroscopic nature of the MgO, a DI rinse was omitted. We found that a $\text{Co}_{1-x}\text{Mn}_x$ film grown directly on MgO resulted in oxidation of the CoMn film and evidence of poor epitaxial growth (loss of the RHEED pattern). To prevent this interaction, a 2 nm Fe buffer layer was used to both stabilize the interface and improve the epitaxial growth. Films were capped with a 3 nm Al layer to prevent oxidation of the metallic surface. Subsequent to these growths, we were able to eliminate the Co oxidation and the need for an Fe buffer layer by changing vendors of our MgO substrates and modifying our cleaning procedure (heating to 850°C for 15 minutes). We grew a select set of compositions without a buffer layer and confirmed that our extracted Co and Mn moments were independent of the presence of the Fe buffer layer.

For all growths, the water cooled Co knudsen cell was held at 1320°C while the Mn oven temperature was varied, ranging from about 690°C to 790°C, to produce samples of different compositions equivalent to a range of a few percent Mn to $x = 0.8$. The 2 nm Fe buffer layer was

deposited with the Fe knudsen cell also held at 1320°C which resulted in a deposition rate of about 0.1 nm/minute. An ideal substrate temperature for growth of Fe on MgO was found to be around 160°C [20], and this was used for both the Fe buffer layer and the $\text{Co}_{1-x}\text{Mn}_x$ growths. The substrate temperature was then reduced to below 100°C for the Al cap layer.

Single-crystal epitaxial growth in the bcc structure was monitored *in-situ* with reflection high-energy electron diffraction (RHEED). Samples with Mn concentrations at and below $x = 0.6$, retained the RHEED pattern for the 4 nm thick growths. In these cases, we did not identify the maximum thickness for film stability beyond 4 nm. Co films grown on GaAs(001) were found to be stable up to between 2 and 38 nm, depending sensitively on growth conditions [21-25]. Above $x = 0.6$ Mn concentrations, the RHEED pattern degraded prior to completion of a 4 nm thick film and thinner alloy films were used.

The quality of the epitaxial growth can be seen by the RHEED pattern shown in Figure 1 for a $\text{Co}_{0.67}\text{Mn}_{0.33}$ film grown on a Fe buffer layer (the Fe buffer layer RHEED pattern is not shown). The RHEED of the CoMn film is taken along the MgO $\langle 100 \rangle$ direction but displays a diffraction structure of the CoMn $\langle 110 \rangle$ direction, confirming that the bcc structure is epitaxial but rotated by 45° compared to the underlying substrate. For compositions above $x = 0.7$, the RHEED displayed additional features indicating a disruption of the bcc structure. These features were present from the initial growth of the CoMn film.

2.2 XPS, XAS and MCD

To determine the composition and investigate the evolution of the electronic structure and the magnetic properties, X-ray measurements were performed at beamlines 4.0.2 and 6.3.1 of the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory. Both the X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (MCD) spectra of the Co and Mn $L_{2,3}$ -edges were performed in the total electron yield (sample current) configuration at room temperature and the MCD was performed in an applied field of 0.05T to 1T with the magnetic field

directed along the photon propagation direction. By comparing the Co and Mn L_{23} -edge XAS integrated peak areas, a precise alloy composition can be made. These relative peak area ratios can be related to the atomic concentrations by comparing the Co:Mn peak area ratios acquired by XAS to the measured x-ray photoelectron spectroscopy (XPS) ratio acquired at the Image and Chemical Analysis Laboratory (ICAL) at Montana State University on select films. XPS measurements of Co and Mn concentrations required Ar sputtering to remove some of the Al capping. Thicknesses were determined from deposition rates calibrated by Rutherford backscattering.

The XAS and MCD spectra for a 4 nm $\text{Co}_{0.75}\text{Mn}_{0.25}$ film deposited on a 2 nm Fe buffer layer grown on MgO(001) is shown in Figure 2. This composition represents the largest measured MCD for Co, corresponding to a 40% enhancement of the MCD intensity over that measured for a pure bcc Co film. The XAS spectra have been normalized to the L_3 peak and the MCD spectra have been corrected for the degree of polarization and the incidence angle. Also shown in the top panel in the long-dashed line is the Co XAS and MCD spectrum for a CoMn film deposited directly on MgO(001) with all other growth conditions held constant. Note the absence of dichroism and the shift and broadening of the L_3 peak. This relatively featureless Co spectrum is not typical of Co oxides where strong, sharp features are indicative of oxidation. The Fe XAS of the 2 nm buffer layer (not shown) is typical of metallic Fe.

3. Moment Variation

The variation of the Co and Mn MCD absolute intensity is shown in Figure 3. At and below $x = 0.6$, the film thickness was 4 nm, above $x = 0.6$ (60% Mn atomic composition), the film thickness was held to ~ 2 nm to maintain the bcc structure. The solid dots are the Co L_3 -edge and the open squares are the Mn L_3 -edge. The error bars used in figure 3 represent the variability of the MCD intensity from multiple measurements taken on the same sample at the same beamline after the sample is removed and replaced into the end-station over the period of a few days. The error bars

associated with a single MCD scan is much smaller (about the size of the data point in the figure). The solid lines represent a linear fit to the data restricted to the appropriate energy range. The Co MCD shows a continuous increase up to $x = 0.24$ where it reaches a maximum enhancement of 40% compared to pure Co. The moment of bcc Co is predicted to be in the $1.7 \mu_B$ range [26 and references therein] whereas measurements find values close to $1.5 \mu_B$ [23]. This corresponds to a maximum Co moment of $2.1\text{-}2.38 \mu_B$ near $x = 0.21$, a value similar or larger than that of bcc Fe. Beyond this peak the Co moment falls linearly with increased Mn content until it abruptly vanishes at $x = 0.7$. The composition of this abrupt moment collapse corresponds to the structural transition that was identified from the RHEED. This abrupt moment loss is also visible in the Mn MCD compositional dependence although the Mn moment is already quite small prior to the collapse.

The onset of Mn moment decay can be determined from extrapolation of the high concentration behavior to lower concentration and is found to occur at nearly the same composition as the Co decay. At lower concentrations, the Mn moment is found to vary markedly. This variability occurs sample to sample, but is also seen at different regions within a single sample (though the composition is shown to be quite homogeneous across the sample). This variability may be due to Mn clustering at the atomic scale, or due to competing interactions that drive the Mn moment alignment [6, 8, 9]. Finally, in the absence of a value for the moment of an isolated Mn atom in a bcc Co host, a determination of the total moment of the system cannot be properly performed. Using calculated values of $3.0 \mu_B$ for the low concentration Mn moment [15], the average moment per atom of the $\text{Co}_{0.76}\text{Mn}_{0.24}$ alloy is in the $2.32\text{-}2.53 \mu_B/\text{atom}$, comparable to the value at the peak of the Slater-Pauling curve.

Conclusions

Thin film $\text{Co}_{1-x}\text{Mn}_x$ single crystals of $x = 0 - 0.7$ were epitaxially deposited on Fe buffer layers grown on single crystal $\text{MgO}(001)$ substrates by MBE. RHEED indicates single crystal bcc growth in registry with the MgO surface but rotated 45° to the surface net. Here, we report on the growth of $\text{Co}_{1-x}\text{Mn}_x$ in the bcc structure on an MgO substrate and on the measurement of enhanced ferromagnetism, stable up to 70% Mn for thicknesses on the order of 4 nm. Initially, both the Co and Mn average moments increase with Mn concentration, with a maximum average moment occurring at 24% Mn, where we find an increase of about 40% in the magnetization above that of pure Co. For an average moment of $1.7 \mu_B/\text{Co atom}$, this corresponds to a Co moment of $2.38 \mu_B/\text{Co atom}$. We have individually measured the average moments of Co and of Mn by the use of soft x-ray magnetic circular dichroism, showing directly that the Mn moments are aligned parallel with Co throughout the ferromagnetic range, and that contrary to the bulk and to fcc thin films, the Co moment itself is enhanced by the alloying of Mn.

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1 column figure

FIGURE 1: RHEED images from the bare MgO(001) substrate taken along the $\langle 100 \rangle$ direction (TOP), for a 3 nm $\text{Co}_{0.67}\text{Mn}_{0.33}$ film on MgO(001) along the $\langle 100 \rangle$ direction of the MgO substrate (CENTER), and along the $\langle 110 \rangle$ direction of the MgO substrate (BOTTOM).

FIGURE 2: Elemental XAS (solid line) and MCD (dashed line) for a 4 nm $\text{Co}_{0.75}\text{Mn}_{0.25}$ film grown on a 2 nm Fe buffer layer on $\text{MgO}(001)$ for the Co L_{23} -edge (TOP) and Mn L_{23} -edge (BOTTOM). Also shown in the top plot is the Co L_{23} -edge XAS spectrum for a CoMn alloy film without the Fe buffer layer (long dashed line). The MCD spectra show that the Mn moment is aligned to the Co moment. Features above 650 eV in the Mn XAS spectra are due to Mg absorption of second order light passed by the monochromator.

FIGURE 3: Compositional dependence for the Co and Mn MCD for a 4 nm $\text{Co}_{1-x}\text{Mn}_x$ film on $\text{MgO}(001)$. For compositions above $x = 0.6$ the film thickness was 2 nm. Solid lines are least-square fits of selected ranges. For $\text{Co}_{0.76}\text{Mn}_{0.24}$, the Co moment is enhanced by 40% compared to the bulk. Both the Co and Mn moment are reduced beyond this peak followed by an abrupt loss of magnetism at $\text{Co}_{0.3}\text{Mn}_{0.7}$.