Nuclear magnetic resonance study of thin Co$_2$FeAl$_{0.5}$Si$_{0.5}$ Heusler films with varying thickness

A. Alfonsov$^1$, B. Peters$^2$, F.Y. Yang$^2$, B. Büchner$^{1,3}$, S. Wurmehl$^{1,3}$

$^1$Leibniz Institute for Solid State and Materials Research IFW, Institute for Solid State Research, 01069 Dresden, Germany
$^2$Department of Physics, The Ohio State University, Columbus, OH 43210
$^3$Institute for solid state physics, Technische Universität Dresden, D-01062 Dresden, Germany

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Abstract

Type and degree of structural order is an important aspect for understanding and controlling the properties of highly spin polarized Heusler compounds. In this work, we compare the structural order and the local magnetic properties revealed by nuclear magnetic resonance (NMR) with the physical properties of thin Co$_2$FeAl$_{0.5}$Si$_{0.5}$ Heusler films with varying thickness. We find a very high degree of $L2_1$ type ordering up to 81% concomitantly with excess Fe of 8 to 13% in the expense of Al and Si. The very good quality as demonstrated by our NMR study suggest that the novel technique of off-axis sputtering technique used to grow the films sets stage for the optimized performance of Co$_2$FeAl$_{0.5}$Si$_{0.5}$ in spintronic devices.

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$^a$ Electronic address: a.alfonsov@ifw-dresden.de
$^b$ Electronic address: s.wurmehl@ifw-dresden.de
I. INTRODUCTION

Spintronics is considered a potential follow-up technology to purely charge-based electronics. In spintronic devices, both charge and spin of electrons are used as information carriers leading to faster switching at lower energy consumption compared to charge-based electronics. Half-metallic ferromagnets (HMFs) represent the optimal materials for spintronics as their conduction electrons are expected to be 100% spin polarized. Heusler compounds with $L2_1$ type structure represent an especially favorable family of predicted HMF compounds and seem to offer all necessary ingredients for their implementation in spintronic devices such as high spin polarization, high Curie temperatures, and a low Gilbert damping constant. However, the observation of the required key spintronic properties in Heusler compounds crucially depends on the type and degree of structural ordering.

Nuclear magnetic resonance spectroscopy (NMR) allows one to probe the local environments of $^{59}$Co nuclei in Co-based Heusler bulk and film samples, and thus enables characterization of local order and quantification of different structural contributions as well as off-stoichiometric composition. Such a local probe of structure and composition is very useful as compounds comprising elements from the same periodic row (e.g. Co and Fe) have very similar scattering factors for x-rays, and thus, x-ray diffraction (XRD) only may not be sufficient to resolve the structural ordering unambiguously.

In addition to information on the chemical, crystallographic environments, NMR techniques are useful to determine the magnetic state of a ferro- or ferrimagnetic material. The restoring field ($H_{\text{rest}}$) is an effective magnetic field originating from a resistance to magnetic oscillations, and therefore is proportional to the square root of the optimal power (i.e. the power producing the maximum spin-echo intensity) of the applied rf pulses during an NMR experiment. $H_{\text{rest}}$ derived in NMR experiments provides a measure of magnetic stiffness or magnetic anisotropy on a local scale, compared with the macroscopic domain wall stiffness contributing to the coercive fields from SQUID magnetometry. The advantage of NMR is that we can measure at a given frequency and can thus relate the magnetic stiffness to a specific local magnetic environment (e.g. phase or structure).

A particular interesting Heusler compound to be mentioned in the context of HMF is Co$_2$FeAl$_{0.5}$Si$_{0.5}$. Band structure calculations predict a high stability of the minority bandgap in this compound. Co$_2$FeAl$_{0.5}$Si$_{0.5}$ has been implemented in thin films and magnetic tunel
junctions. Recently, we have epitaxially grown Co$_2$FeAl$_{0.5}$Si$_{0.5}$ films on lattice-matched MgAl$_2$O$_4$ (001) substrates by a novel off-axis sputtering technique yielding films with an exceptionally high quality. In this work, we characterize the local crystallographic and magnetic structure of those films as a function of film thickness using NMR. We were able to relate the macroscopic physical properties of those Co$_2$FeAl$_{0.5}$Si$_{0.5}$ films to the local ordering.

II. EXPERIMENTAL DETAILS

Epitaxial Co$_2$FeAl$_{0.5}$Si$_{0.5}$ films were grown on MgAl$_2$O$_4$ (001) substrates by off-axis sputtering in a UHV system with a base pressure as low as $7 \times 10^{-11}$ Torr using ultra-pure Ar (99.9999%) as sputtering gas. Optimal quality Co$_2$FeAl$_{0.5}$Si$_{0.5}$ epitaxial films were obtained at an Ar pressure of 4.5 mTorr, a substrate temperature of 600°C, and DC sputtering at a constant current of 12 mA, which results in a deposition rate of 5.6 Å/min. The Co$_2$FeAl$_{0.5}$Si$_{0.5}$ epitaxial films were characterized by a Bruker D8 Discover high-resolution triple-axis x-ray diffractometer (XRD). Details about growth and characterization are found elsewhere.

The NMR experiments were performed at 5 K in an automated, coherent, phase sensitive, and frequency-tuned spin-echo spectrometer (NMR Service Erfurt, Germany). We used a manganin coil wrapped around the sample to apply and pick up the rf pulses. This coil is implemented in an LC circuit with three capacitors. The NMR spectra were recorded at 5 K in the frequency ($\nu$) range from 104-254 MHz in steps of 0.5 MHz in zero magnetic field. All NMR spectra shown here were corrected for the enhancement factor as well as for the $\nu^2$ dependence, resulting in relative spin-echo intensities which are proportional to the number of nuclei with a given NMR resonance frequency.

III. RESULTS AND DISCUSSION

Figure 1 shows the $\theta/2\theta$ scan of a 45-nm thick Co$_2$FeAl$_{0.5}$Si$_{0.5}$ epitaxial film on MgAl$_2$O$_4$ (001). The clear Laue oscillations near the Co$_2$FeAl$_{0.5}$Si$_{0.5}$ (004) peak demonstrate the high crystalline uniformity as well as smooth surface and sharp interface with the substrate. Fig. 1(b) presents a rocking curve of the (400) peak with a full-width-at-half-maximum (FWHM) of 0.0043°, which is at the instrumental resolution limit of our high-resolution
FIG. 1. (a) High resolution $\theta/2\theta$ XRD scan of a 45-nm Co$_{2}$FeAl$_{0.5}$Si$_{0.5}$ (CFAS) film grown on MgAl$_{2}$O$_{4}$ (001) substrates. (b) XRD rocking curve of the (004) peaks of the Co$_{2}$FeAl$_{0.5}$Si$_{0.5}$ film gives a FWHM of 0.0043°.

XRD system, revealing exceptional crystalline quality.

We measured the $^{59}$Co NMR spectra for different thin film samples with varying thickness (20, 45, 84, 120 and 200 nm) in order to further characterize the structural quality of our films. Fig. 2 exemplarily shows the normalized $^{59}$Co NMR spectra of films with thickness $t = 20, 84$ and 200 nm in comparison with that of a Co$_{2}$FeAl$_{0.5}$Si$_{0.5}$ bulk sample (data taken from Ref. 29). All spectra share the main line around 163 MHz with one shoulder on the low frequency side and two pronounced satellites on the high frequency side. Using a simple model with three Lorentzian lines of equal linewidth and spacing to fit the measured NMR spectra, we obtained the average spacing of 33 MHz between the main line and the high frequency satellites, which is slightly larger than in the corresponding bulk samples (31 MHz)$^{29}$.

The observation of low and high frequency satellite lines with a spacing of about 30-33 MHz suggest contribution from $B2$ type ordering of the films, in line with the interpretation of the NMR data for Co$_2$FeAl$_{0.5}$Si$_{0.5}$ and Co$_2$FeAl bulk samples$^{12,29}$. However, the satellite on the low frequency side is considerably more pronounced in the bulk sample than in the films while the high-frequency satellites are less pronounced in the bulk sample suggesting that the films are more Fe-rich and Al/Si-poor than the expected 2:1:0.5:0.5 stoichiometry (compare$^{13,29}$). The formation of Fe-rich environments may also be responsible for the slightly higher than expected magnetic saturation-moment.
FIG. 2. (Colour online) Normalized $^{59}$Co NMR spectra of Co$_2$FeAl$_{0.5}$Si$_{0.5}$ thin films with thicknesses of $t = 20, 84, \text{ and } 200$ nm in comparison with the NMR data of a Co$_2$FeAl$_{0.5}$Si$_{0.5}$ bulk sample$^{29}$.

FIG. 3. (Colour online) Thickness dependence of NMR resonance frequency (blue squares, left side) and square root of the optimal power (red circles, right side) for the main line (163 MHz) of the $^{59}$Co NMR spectrum.

In the following, we will explore the trends in the NMR data of the films in comparison with their properties.

Figure 3 shows the thickness dependence of the NMR resonance frequency (blue squares, left side) and square root of the optimal power (red circles, right side). The NMR resonance frequency of the main line was estimated from a Lorentzian fit to the NMR main line (163 MHz) of the $^{59}$Co NMR spectrum. There is a clear transition in Fig. 3 from lower to higher resonance frequencies at thicknesses between 84 and 120 nm. Similarly, there is
a clear transition for optimal power at thicknesses between 84 and 120 nm (red dots in Fig. 3). The measurement of optimal power (i.e. the power producing the maximum spin-echo intensity) of the applied rf pulses allows to indirectly investigate the magnetic stiffness or magnetic anisotropy on a local scale\textsuperscript{10,17} with the square root of the optimal power being proportional to the restoring field. The transition for both the resonance frequencies and the optimal power at thicknesses between 84 and 120 nm may be related to the fact that the Co\textsubscript{2}FeAl\textsubscript{0.5}Si\textsubscript{0.5} films are mostly strained at thicknesses below 100 nm and start to relax above 100 nm as observed by XRD. For the 200-nm film, the restoring field reaches the value for the bulk sample.

A comparison between the NMR spectra of Co\textsubscript{2}FeAl\textsubscript{0.5}Si\textsubscript{0.5} bulk samples\textsuperscript{29} and thin films (Fig. 2) suggest the presence of both \textit{L}2\textsubscript{1} and \textit{B}2 type order. In order to perform a detailed quantitative analysis of the different contributions to the NMR spectra, we fitted the NMR spectra of all samples using a sum of Gaussian lines. The corresponding parameters of these lines, such as resonance frequency, linewidth, and intensity, were constrained according to a model similar to the one described in detail in Ref.\textsuperscript{29}.

For \textit{L}2\textsubscript{1} type order only one NMR line is expected, while \textit{B}2 type order yields several NMR lines\textsuperscript{10,12}. Hence, in the presence of both \textit{L}2\textsubscript{1} and \textit{B}2 type order and off-stoichiometry, the relative area of the NMR spectra can be represented as a sum of several lines originating in different structural and compositional contributions. The spacing between adjacent resonance lines, $\Delta B2$, may be assumed to be a constant while their relative contribution to the NMR spectrum is given by the amount of random mixing of Fe and Al/Si on one crystallographic site (\textit{B}2 order) as well as by the Fe to Al/Si ratio. The off-stoichiometry between Fe and Al/Si contributes to NMR lines on the high frequency side only due to the extra Fe at the Al/Si sites in the first Co shell. From the relative areas of these lines, the amount of off-stoichiometry and \textit{L}2\textsubscript{1}/\textit{B}2 type order in the films can be quantified. Due to the random mixing of Al and Si on one (\textit{L}2\textsubscript{1} plus off-stoichiometry) or two (\textit{B}2 plus off-stoichiometry) crystallographic sites, each NMR line further broadens or splits into a set of sub-lines with equal spacing $\Delta Al/Si$ between them. For the quantification and interpretation of the measured NMR spectra, we fit each spectrum using a sum of Gaussian lines and compare their relative areas to the probabilities calculated from a random atom model\textsuperscript{29}, which is mathematically expressed in form of a binomial distribution function:
\[ P(n, m, l, k, x, y, C_{B2}, C_{L21}) = C_{B2} \cdot \frac{N!}{n!(N - n - m)!m!} (1 - x)^{N-m-k} x^m y^k (1 - y)^{N-n-k} + \]
\[ C_{L21} \cdot \frac{L!}{l!(L - l - k)!k!} (1 - u)^{L-l} u^l y^k (1 - y)^{(L-l-k)} \delta_{n,4} \]

with \( \delta_{n,4} \) defined as:
\[
\delta_{n,4} = \begin{cases} 
1, & \text{if } n = 4 \\
0, & \text{if } n \neq 4 
\end{cases}
\]

The first term in Eq. 1 represents the \( B2 \) contributions with a random distribution of Fe and Al/Si, where \( C_{B2} \) is the degree of \( B2 \) type order. This random distribution involves both the 4a and 4b Wyckhoff positions of the respective \( L2_1 \) lattice, which correspond to the 1b position in the \( B2 \) notation. In Eq. 1, \( x \) represents the Fe to (Al+Si) stoichiometry, giving rise to calculating the probability of finding Fe atoms on the \( Z \) (Al and Si) sites; \( y \) denotes the Al to Si stoichiometry \( (Al_ySi_{1-y}) \). For stoichiometric \( Co_{2}FeAl_{0.5}Si_{0.5} \) films with complete \( B2 \) type order, \( x = 0.5 \) while \( x > 0.5 \) indicates off-stoichiometry with Fe excess. Here, \( N = 8 \) is the number of possible sites for atoms in the first Co shell while \( n, m, \) and \( k \) are the corresponding numbers of Fe, Si, and Al atoms, respectively, in the first Co shell. The second term in Eq. 1 represents the contribution from \( L2_1 \) type order, \( u \) is the amount of Fe to (Al+Si) off-stoichiometry \( (u = 0 \) for stoichiometric composition\), \( L \leq 4 \) is the number of possible sites for Fe atoms on the Al/Si sites in the first Co shell, \( l \) and \( k \) are the numbers of Fe and Si/Al atoms in the first shell, respectively. Since both \( x \) and \( u \) represent the off-stoichiometry, there is a relation between these two parameters \( x = 0.5 \ u + 0.5 \). The coefficient \( C_{B2} \) and \( C_{L21} \) represent the relative contribution from \( ^{59}Co \) nuclei with a \( B2 \) and \( L2_1 \) first shell environment, respectively, and \( C_{B2} + C_{L21} = 1 \).

Figure 4 shows the fitting result of the NMR spectrum for the 84 nm \( Co_{2}FeAl_{0.5}Si_{0.5} \) films, where \( y, u, C_{B2}, \Delta Al/\Si, \) and linewidths of individual Gaussian lines are fitting parameters while the NMR resonance frequencies and the spacing between lines \( \Delta B2 \) were taken from the Lorentzian fit described above. The residual fit mismatch for all spectra does not exceed 15% which is quite good for such a rather simple model. The spacing \( \Delta Al/\Si \) between lines due to the mixing of Al and Si is found to be about 7 MHz, which is very similar to the bulk sample. In addition, the fit yields the Al to Si ratio of 1 as expected.
FIG. 4. (Colour online) Normalized $^{59}$Co NMR spectrum a 84-nm thick Co$_2$FeAl$_{0.5}$Si$_{0.5}$ film, fitting (red curve). Analysis of the data gives a an degree of $L_2^1$ order of 81%.

FIG. 5. (Colour online) NMR linewidth (black squares) and $L_2^1$ type order contribution (red open circles) as a function of film thickness.

Our results confirm a quite high degree of order for all film thicknesses (Fig. 5). The highest degree of $L_2^1$ order is found to be as high as 81% for the 84 nm film. In order to further check our analysis, we compare the trend in NMR linewidth for all films as function of thickness.

Generally, the NMR linewidth reflects the degree of ordering in a given sample. Figure 5 shows that the linewidth decreases with increasing film thickness, indicating an improvement of ordering in thicker films. Generally, the dependence of the NMR linewidth reflects the evolution of $L_2^1$ ordering, as expected. In particular, there is a local minimum for the 84 nm
FIG. 6. Fe/(Al+Si) off-stoichiometry of the Co$_2$FeAl$_{0.5}$Si$_{0.5}$ films as a function of resonance frequency of the main NMR line, which show excess Fe of 8 to 13% in the expense of Al and Si.

film which has a linewidth for 8.1 MHz. Similarly, the degree of $L_2$ ordering increases with film thickness, except that the 84-nm film exhibits the highest $L_2$ ordering of 81%, which correlates with the NMR linewidth. This finding suggests that the 84 nm film has the best quality among other films in the series, which may be explained as follows. In general, the structural quality and $L_2$ ordering improve as film thickness increases. The Co$_2$FeAl$_{0.5}$Si$_{0.5}$ films under 100 nm thick are totally strained with tetragonal distortion and remain structurally uniform; while above 100 nm, the films start to relax, which introduces change and inhomogeneity in crystal structure. Consequently, the best structural quality with the highest $L_2$ ordering is observed in the largest available thickness below 100 nm, i.e., 84-nm Co$_2$FeAl$_{0.5}$Si$_{0.5}$ film.

Besides $B2$ type ordering, we also observe excess Fe in the expense of Al and Si, which manifests in the significant enhancement of the high frequency NMR lines. We were able to quantify this off-stoichiometry by fitting the data with eq. Fig. 6 shows the Fe to Al/Si off-stoichiometry as the function of resonance frequency of the NMR main line, indicating 8 to 13% excess Fe in the films. The frequency shift originates from the changes of the transferred hyperfine fields along with changes in the macroscopic magnetic moments due to excess Fe.
IV. SUMMARY

We presented a detailed NMR analysis of the structural and local magnetic properties of Co$_2$FeAl$_{0.5}$Si$_{0.5}$ films with varying thickness. Using NMR, we are able to quantify the amount of $L2_1$ ordering along with the quantification of the Fe:Al/Si off-stoichiometry. All results confirm the excellent quality of the Co$_2$FeAl$_{0.5}$Si$_{0.5}$ films which supports our claim that the novel technique of off-axis sputtering used to grow those films may further advance the quality of Heusler films towards optimized performance in spintronic devices.

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