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Local formation of a Heusler structure in CoFe–Al alloys

S. Wurmehl,^{1,a)} P. J. Jacobs,² J. T. Kohlhepp,² H. J. M. Swagten,² B. Koopmans,² S. Maat,³ M. J. Carey,³ and J. R. Childress³

¹Institute for Solid State Research, IFW Dresden, P.O. Box 270116, D-01171 Dresden, Germany

²Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

³San Jose Research Center, Hitachi GST, 3403 Yerba Buena Road, San Jose, California 95135, USA

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We systematically study the changes in the local atomic environments of Co in CoFe–Al alloys as a function of Al content by means of nuclear magnetic resonance. We find that a Co₂FeAl Heusler type structure is formed on a local scale. The observed formation of a highly spin-polarized Heusler compound may explain the improved magnetotransport properties in CoFe–Al based current-perpendicular-to-the-plane spin-valves. © 2011 American Institute of Physics.

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Current perpendicular-to-the-plane giant magnetoresistive (CPP-GMR) read heads are being considered as a follow-up technology for tunnel magnetoresistive read heads.^{1,2} A crucial issue for the success of such devices is to further enhance the GMR ratio particularly at room temperature. In this context, highly spin-polarized materials are promising candidates to increase the bulk spin-scattering asymmetry and to enhance the (CPP-)GMR. Band structure calculations have shown that various Heusler compounds exhibit 100% spin polarization at the Fermi level.³ Thus, the implementation of Heusler compounds in CPP-GMR spin-valves seems desirable.^{4–6} However, annealing temperatures higher than 300 °C which are usually necessary to obtain the highly ordered L2₁ phase are incompatible with reliable device fabrication. An enhancement of the CPP-GMR was also observed by addition of Al to a CoFe alloy, even with a low annealing temperature T ~ 250 °C.^{1,2} The composition with highest MR was found to be (Co₅₀Fe₅₀)₇₅Al₂₅.² The authors concluded that the addition of Al to CoFe increases the resistivity of the magnetic layers while maintaining a high degree of bulk spin-dependent scattering that leads to an enhanced GMR signal. In order to further optimize CoFe–Al spin-valves, it is important to understand the impact of the Al alloying on the local and electronic structure. In this paper, we report on a study of the local chemical structure of (CoFe)_{1-x}Al_x films used for CPP-GMR spin-valves by means of spin echo nuclear magnetic resonance (NMR). The sensitivity of NMR even to small changes in the local (magnetic and electronic) environment makes NMR an ideal method to determine the local modifications upon addition of Al.^{7,8} Here, we demonstrate the local formation of a Heusler-like structure by addition of Al to a CoFe alloy. The observed local ordering is apparently correlated with the observed enhancement of the GMR effect.

See supplementary material and Refs. 2,7,8 for experimental details.⁹

In order to separate the contribution of Al on the local structure from the pure CoFe contributions, we also studied nominal CoFe samples as a reference. The composition of the CoFe sample was determined by XRF analysis to be 51.6 ± 0.5 at. % Co and 48.4 ± 0.5 at. % Fe. In the case of a perfectly ordered structure for Co₅₀Fe₅₀, the formation of a

B2 type lattice (CsCl type) is expected with exactly eight Fe next neighbors for each ⁵⁹Co nucleus. However, previous NMR measurements of Co₅₀Fe₅₀ alloys indicated the formation of a body centered cubic (bcc) lattice¹⁰ with a random distribution of Co and Fe atoms. In such a randomly ordered alloy, the first coordination sphere of the NMR active ⁵⁹Co nuclei consists of eight atoms. The random intermixing of Co and Fe creates nine possible configurations (8Co+0Fe, 7Co+1Fe, ..., or 0Co+8Fe) for the first nearest neighbor shell of a ⁵⁹Co nucleus. The random distribution of Co and Fe is mathematically described by a binomial distribution. The probability $P(n, x)$ of finding a particular environment is given by $P(n, x) = \{N! / [(N-n)!n!]\} (1-x)^{N-n} x^n$, with $N=8$ corresponding to the number of possible sites in the first shell of Co and x representing the ratio of the Fe atoms. Here, we used the ratio found by XRF ($x=0.48$). $P(n, x)$ can be directly compared to the relative areas of the resonance lines of a spin echo NMR measurement, while the corresponding resonance frequencies are related to the hyperfine fields of the active atom in this particular environment.

Figure 1(a) shows the ⁵⁹Co NMR spectrum of the CoFe sample (black dots), the resulting Gaussian lines corresponding to the fitted individual local CoFe environments (black lines) and the fit using the sum of Gaussian lines (gray line). The widths of the Gaussian lines were constrained to be

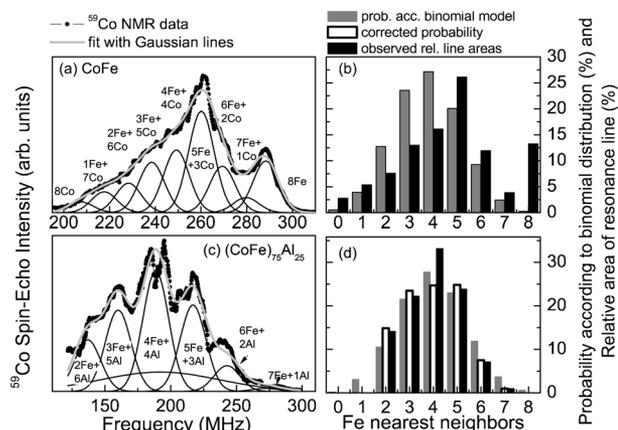


FIG. 1. ⁵⁹Co NMR spectrum of pure CoFe (0 at. % Al) (a) the ⁵⁹Co NMR spectrum of the CoFe–Al sample (25 at. % Al) (c) and the corresponding fit with Gaussian lines. The right panels (b) and (d) show a comparison between the random atom model and the relative areas of each resonance line in the fit.

^{a)}Electronic mail: s.wurmehl@ifw-dresden.de.

equal as the width is due to higher order effects that average out across the sample.^{8,10} The fit yields an overall line width of 11.0 ± 0.5 MHz. All frequencies for certain local environments are found to agree well with those observed by Jay *et al.*¹⁰ Figure 1(b) shows a comparison between the relative areas of the Gaussian lines and the probability according to the binomial model. For a 1:1 stoichiometry, this model predicts a preferred environment of 4Fe+4Co atoms that correspond to the peak at 249 MHz. By contrast, the main resonance line is found at 260 MHz (5Fe+3Co local neighbors). Moreover, the line at 288 MHz (eight Fe neighbors) is much more prominent than expected assuming a perfect random distribution of Co and Fe and hints at preferential ordering. The corresponding atomic environment for this line consists of eight Fe atoms in the first shell and, thus, corresponds to an ordered *B2* type lattice. The enhancement of this line was also observed by Jay *et al.*¹⁰ Thus, there seems to be a mixture between a random distribution and a locally ordered environment, which is perhaps the result of the CoFe layer being sputtered and subsequently vacuum annealed for 5 h at 518 K, allowing some of the atoms to arrange themselves in the observed preferred environment (see supplementary material for details about the NMR spectrum of the additionally annealed sample).⁹ Thus, the as-prepared CoFe alloy prefers the randomly ordered bcc structure and gradually orders in the *B2* lattice upon additional annealing. These spectra give a good indication of what a CoFe alloy would look like in a CoFe–Al sample.

In order to follow the local changes upon addition of Al to CoFe, we measured several samples with different CoFe–Al compositions. Figure 1(c) shows the ⁵⁹Co NMR spectrum of a sample with 25% of Al in more detail. For this sample, the XRF analysis determined a composition of 38.52 at. % Co, 36.27 at. % Fe, and 25.21 at. % Al. This is also the composition that was found to exhibit the highest magnetoresistance within the Al series.² Assuming that Co, Fe, and Al form an *A2* bcc alloy, in which all atoms are randomly distributed over the lattice, this would lead to one broad line located around 190 MHz without pronounced peaks^{8,11} as the hyperfine fields and the resonance lines of the local environments with different numbers of Co, Fe, and Al neighbors would overlap. Instead, one clearly observes six distinct lines with a substructure and a broad “background” line. Note that due to technical limitations, only measurements above 100 MHz are possible. The clear observation of distinct main lines points to a higher degree of order than the completely randomly ordered *A2* type structure.

For a discussion about possible structure types for ternary alloys and their related NMR spectra see Ref. 9.

The six resonance lines observed in Fig. 1(c) and the main resonance line found at 190 MHz are in good agreement with the main resonance found for a *B2* type ordered Co₂FeAl Heusler compound.^{8,11,12} This peak at 190 MHz corresponds to local environments with 4Fe+4Al neighbors. Higher frequency peaks correspond to Fe rich environments while lower frequency peaks correspond to Al rich environments.^{8,11,12} The mean spacing between adjacent resonance lines is similar to those found for a *B2* ordered Co₂FeAl Heusler compound (27 MHz). Seemingly, the NMR spectrum of the ternary CoFe–Al alloy exhibits the characteristics of the corresponding *B2* ordered Heusler compound. In particular, the best fit was obtained by assuming six reso-

nance lines representing a *B2* type structure in addition to a broad resonance line. This broad line represents *A2* type contributions of a completely disordered CoFe–Al alloy, which is similar to the one found in a Co₂FeAl Heusler sample with a mixture of *A2* and *B2* contributions.⁸ Moreover, the line at 190 MHz is more prominent than expected for a pure *B2* type ordering (see Ref. 8) that points to a preferential enhancement of the 4Fe+4Al environment. In line with the considerations above and Ref. 8, the considerations above, this enhancement points to the formation of *L2*₁ environments on a local scale. It may be concluded that the spectrum of the CoFe–Al alloy consists of a mixture of the *A2*, *B2*, and *L2*₁ Heusler type structure. To confirm and quantify, we compared the observed areas of the Gaussian lines (black bars) and the probability according to the binomial model in two ways excluding (gray) and including (white) *A2* and in particular *L2*₁ contributions as described in Ref. 8, (Fig. 1(d)). It clearly indicates that the NMR spectrum of the CoFe–Al alloy closely follows the binomial distribution expected for a *B2* type ordered Co₂FeAl Heusler compound with about 19% of *A2* type contributions and about 3% of *L2*₁ contributions. The additional substructure of the main lines originates in higher shell effects.⁸

Figure 2 shows the ⁵⁹Co NMR spectra for (CoFe)_{1-x}Al_x samples with different Al contents. The same fitting procedures as described above were applied to all spectra except for the 19% Al sample where the line at 243 MHz has a much smaller line width of 7 MHz (compared to roughly 18 MHz for all other lines). The (CoFe)_{1-x}Al_x spectra show pronounced peaks that can be attributed to different local environments for the ⁵⁹Co nuclei. These peaks were fitted by Gaussian lines, leading to an overall fit of the spectrum by the sum of all Gaussian lines (gray line). The measurements show a clear trend of decreasing NMR frequencies for increasing Al content up to 22 at. % in agreement with Ref. 12 showing that in Co₂FeAl, the Fe rich environments are on the high frequency side, while Al in the first shell decreases the resonance frequency of ⁵⁹Co nuclei. The black lines in Fig. 2 indicate the positions of the line at 190 MHz (4Fe+4Al local neighbors) and the line at 280 MHz (8Fe+0Al neighbors configuration in the Al free CoFe alloy). It is clear, however, that the addition of Al to CoFe leads to a drastically different local structure than bcc CoFe and that the contribution of bcc CoFe quickly becomes negligible even for small amounts of Al, as demonstrated by the appearance of the 190 MHz line (see Fig. 2). The observation of pronounced lines also excludes a random distribution of all atoms in the CoFe–Al alloy and can be attributed to different local environments for the ⁵⁹Co nuclei and therefore to a higher degree of order.

The spectra of the 8% and 19% samples are a superposition of the resonance lines originating in the formation of a local Heusler type structure and a randomly ordered CoFe structure and there is a clear decrease of the 280 MHz line corresponding to only eight Fe neighbors compared to the 0% sample. This is expected considering that Al neighbors will enter the higher coordination shells, which will destroy the preferential ordering of the pure Fe coordination compared to the pure CoFe alloy. A clear fingerprint of the resonance lines of a Heusler type ordering is observed for the 22%, 25%, and 28% samples (compare Refs. 8, 11, and 12). Thus, with the addition of Al, CoFe has a tendency to form a

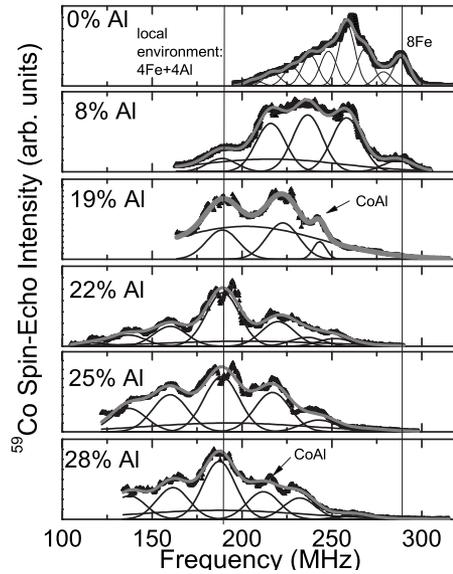


FIG. 2. ^{59}Co NMR spectra for the $(\text{CoFe})_{1-x}\text{Al}_x$ samples.

Heusler compound. In a few of the samples, there is also a noticeable preference for the $L2_1$ ordering with preferred first nearest neighbor shell with $4\text{Fe}+4\text{Al}$ atoms. Two spectra (19% and 28%) exhibit an additional line in the range of 200–250 MHz with a smaller line width than the line widths attributed to the CoFe and Heusler resonances (indicated by arrows in Fig. 2), which might originate from a formation of a Co–Al alloy.¹³ It is worth noting that formation of a Fe–Al alloy would not be detected in the available frequency range, even though it might also be present in the samples. On the other hand, the precipitation of a CoFe alloy is definitely excluded.

The most important question is whether these structural results are correlated with the enhanced GMR.² In order to establish such a relation, we compared the $L2_1$ and $B2$ type contributions for different samples with the CPP-GMR ratios measured by Maat *et al.* on $(\text{CoFe})_{1-x}\text{Al}_x$ spin-valves (black squares in Fig. 3). The dotted line indicates the sample with 0% Al (no Heusler contribution) and hence the CPP-GMR ratio of the pure CoFe alloy. According to Fig. 3, the CPP-GMR ratio and the formation of a highly spin-polarized Heusler compound seemingly follow a similar trend upon Al addition. In particular, the highest GMR ratios are obtained for those Al contents that also show a high $B2$ and $L2_1$ type contribution (samples with 22% and 25% Al). The CPP-GMR is lower in the samples with lower Al content (19%, 8%, and 0% Al) for which the contribution of a Heusler compound is also found to be low by means of NMR. The sample with 28% Al shows a comparably high Heusler contribution but a low CPP-GMR ratio. This might be attributed to the observed Co–Al separation, leading to additional spin-scattering contributions followed by a decrease of the CPP-GMR ratio. In particular, it should be noted here that the CPP-GMR will also depend on such parameters the thickness of the layers, spin-diffusion length, interfacial scattering, and growth imperfections such as atomic interdiffusion across interfaces.

The clear observation of the characteristics of both $B2$ and $L2_1$ contributions to the spectrum confirm the local formation of a Heusler compound upon addition of Al. Co_2FeAl in the $B2$ type structure is predicted to conserve the high spin

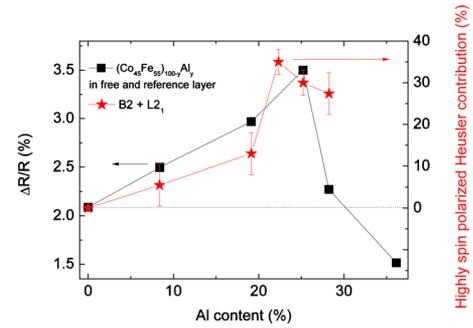


FIG. 3. (Color online) Comparison between the CPP-GMR properties (Ref. 2) and the contribution of highly spin-polarized Heusler compound both as a function of the Al content of the $(\text{CoFe})_{1-x}\text{Al}_x$ samples.

polarization^{14–16} assumed for Co_2FeAl in the $L2_1$ type structure and consequently, the bulk spin-scattering asymmetry in the CPP-GMR spin-valves.

In summary, we systematically studied the changes in local environments upon addition of Al to the CoFe alloy in CPP-GMR multilayers by means of NMR. We have established that a Co_2FeAl Heusler type structure is formed on a local scale. The formation of a high spin polarization upon $B2$ and $L2_1$ type ordering is seemingly related to the observed improvement of the magnetotransport properties. For further performance increases with CoFe–Al, the chemical order needs to be improved further toward $L2_1$ and $B2$ ordering, which however may require higher-temperature annealing. Practical limits on the annealing of recording head wafers ($\approx 300^\circ\text{C}$) create a challenge in implementing such improvements without other negative effects.

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⁹See supplementary material at <http://dx.doi.org/10.1063/1.3517490> for experimental details, details of the NMR spectra of CoFe and additionally annealed CoFe, possible structure types for ternary alloys and their related NMR spectra, and the possible Co–Al separation.

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