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Citation for published version (APA):

Wurmehl, S., Kohlhepp, J. T., Swagten, H. J. M., & Koopmans, B. (2012). 59Co nuclear magnetic resonance study of the local distribution of atoms in the Heusler compound Co₂FeAl_{0.5}Si_{0.5}. *Journal of Applied Physics*, 111(4), 043903-1/8. [043903]. <https://doi.org/10.1063/1.3684686>

DOI:

[10.1063/1.3684686](https://doi.org/10.1063/1.3684686)

Document status and date:

Published: 01/01/2012

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Citation: *J. Appl. Phys.* **111**, 043903 (2012); doi: 10.1063/1.3684686

View online: <http://dx.doi.org/10.1063/1.3684686>

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^{59}Co nuclear magnetic resonance study of the local distribution of atoms in the Heusler compound $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$

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(Received 5 October 2011; accepted 11 January 2012; published online 17 February 2012)

In this work, the spin-echo nuclear magnetic resonance (NMR) technique is used to probe the local structure of $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ bulk samples. The ^{59}Co NMR spectrum of the Heusler compound $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ consists of four main resonance lines with an underlying sub-structure. The splitting into the main resonance lines is explained by contributions of the $B2$ type structure. The sub-lines are attributed to a random distribution of Al and Si. By comparing the experimental results with an appropriate multinomial distribution, the fraction of the Al/Si intermixing and the ratio between the contributing structure types is assigned. The main structural contribution of as-cast bulk samples is of $B2$ type with 38% of $L2_1$ contributions. The $L2_1$ contribution can be enhanced to 59% by an appropriate annealing process. However, $B2$ contributions are still present after annealing. Additional foreign phases such as fcc-Co and Co-Al, with relative contributions of less than one percent, are also found in both as-cast and annealed samples. Resonance lines related to slight amounts of the ternary, parental Heusler compounds Co_2FeAl and Co_2FeSi are also observed. © 2012 American Institute of Physics. [doi:10.1063/1.3684686]

I. INTRODUCTION

Tunnel junctions using the quaternary compound $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ have already been successfully grown and investigated^{1–7} in the $L2_1$ or $B2$ structure, leading to tunneling magnetoresistance (TMR) ratios of up to 220% at ambient temperature. This high TMR ratio is actually expected from the particular high stability of the minority bandgap predicted for $\text{Co}_2\text{FeAl}_{1-x}\text{Si}_x$ Heusler compounds with $x \sim 0.5$.^{8,9}

Bulk samples of the quaternary members of the substitutional series $\text{Co}_2\text{FeAl}_{1-x}\text{Si}_x$ exhibit the $L2_1$ structure for $x \geq 0.4$ and the $B2$ structure for compounds with $x < 0.4$, as recently shown by Balke *et al.* using powder x-ray diffraction (XRD).¹⁰ Nakatani *et al.*¹¹ reported a mixture of 10% $A2$ and 20% $B2$ contributions within the $L2_1$ structure, also using XRD.

In this work, ^{59}Co nuclear magnetic resonance (NMR) was used to investigate $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ bulk samples as the most prominent representative of the complete substitutional series. NMR probes the local environments of the NMR active atoms and is thus able to resolve next neighbor interactions. This makes NMR an ideal tool to determine the local distribution of Al and Si in $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$. As will be shown in the following, the bulk NMR spectra reveal a splitting into four main and several sub-lines. The main lines originate from the distribution of Fe and (Al, Si) in the neighboring shell of the ^{59}Co nuclei and are described in terms of a $B2$ type structure with contributions of the $L2_1$ type structure, while the sub-lines are assigned to a random distribution of Al and Si. Note, that a distribution of only the

Al and Si atoms leads to a higher symmetry and to the $L2_1$ structure, which is an ordered variant of the $B2$ structure. The annealed sample used in this NMR study is exactly the same sample as used in Ref. 10.

The paper is organized as follows: starting with a short introduction to the experimental details, a discussion of the relevant structural models and the expected NMR spectra will be presented in Secs. III and IV. These structural models will be used in Sec. V to explain the observed NMR spectra of as-cast and annealed $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ bulk samples.

II. EXPERIMENTAL DETAILS

The NMR experiments were performed at 4.2 K in a home-build, automated, coherent, phase-sensitive, and frequency-tuned spin-echo spectrometer. Pulse lengths of 0.5 μs were used. In order to apply and pick up the rf pulses, a copper coil was wrapped around the sample. This coil is implemented in an LC-circuit with two capacitors. The reflection of the rf signal is avoided by adjusting these capacitors to an impedance of 50 Ω . After filtering and amplifying, the signal is split into two signals with a phase shift of 90° and demodulated, followed by a Fourier transformation, which leads to the intensity of the signal. The NMR spectra were recorded in the frequency (ω) range from 110 to 250 MHz in steps of 0.25 MHz. No external field was applied. All NMR spectra shown here were corrected for the enhancement factor as well as the ω^2 dependence, resulting in relative spin-echo intensities which are proportional to the number of nuclei with a given NMR resonance frequency. The enhancement correction was experimentally done by monitoring at every frequency the spin-echo intensity as a function of the applied rf power. With this procedure, the optimum rf power was found, from which the enhancement

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factor was determined, and consequently the data were corrected for this enhancement (see e.g., Refs. 12 and 13). The correction for the frequency dependence was done by dividing the spin-echo intensity by ω^2 . The inter-pulse duration was $5\mu\text{s}$, which is between one and two orders of magnitude smaller than the spin-spin relaxation time measured over the whole spectrum range. Thus, a correction for the spin-spin relaxation time was not necessary in this study.

Two types of polycrystalline $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ Heusler compound bulk samples were provided by the group of C. Felser (Johannes Gutenberg-Universität, Mainz); the sample preparation and characterization are described in Ref. 10. The first sample type comes directly from the arc-melting process. This sample will be referred to as cast sample. The second type was annealed at 873 K for 26 d and will be referred to as annealed sample. Note that the annealed sample used in this NMR study is exactly the same sample used in Ref. 10.

III. STRUCTURAL MODELS

The Heusler compound $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ represents a quaternary compound with an overall stoichiometry of $\text{X}_2\text{YZ}_{1-x}\text{Z}'_x$ and is reported to exhibit the $L2_1$ type structure as well as the $B2$ type structure^{1-3,10,11} (see Fig. 1(a)).

The crystal lattice for the Heusler structure is of Cu_2MnAl type, with the corresponding space group $Fm\bar{3}m$ ($L2_1$ type structure). In the case of a ternary Heusler compound with overall stoichiometry X_2YZ , the first coordination shell of the X atom (Wyckoff position 8c) in the $L2_1$ structure type consists of 4Y (Wyckoff position 4b) + 4Z (Wyckoff position 4a) atoms. Thus, there is only one particular first shell environment for the X atoms.

A partial substitution of the Z (Al) atom by Z' (Si) leads to a quaternary compound with the overall stoichiometry $\text{X}_2\text{YZ}_{1-x}\text{Z}'_x$. Consequently, this substitution will change the first coordination shell of the X atom, which is at the origin (see Fig. 1(a)). Under the assumption that the Z' atoms randomly replace some of the Z atoms, one expects that the central X atom can be surrounded either by 4Y + 0Z', 3Z + 1Z', 2Z + 2Z', 1Z + 3Z', or 0Z + 4Z' nearest neighbors, leading to five different first shell environments.

An ordered variant of the $L2_1$ structure is the $B2$ structure with a lower symmetry (space group $Pm\bar{3}m$, CsCl type crystal lattice); here a mixture of the Y(Fe) and Z(Al, Si) atoms occurs. In case of a complete intermixing, the Y and Z sites become equivalent and the site occupancy factors of the 1a position (4a and 4b positions of the $L2_1$ structure) are 0.5 for both Y and Z atoms (see Fig. 1(b)). The first coordination sphere of the X atom (Wyckoff position 1b) of the $B2$ type structure consists of 8 atoms, which are either Y or Z (see Fig. 1(a)). Thus, there are nine different possibilities for the first shell environment in case of a $B2$ type structure corresponding to 8Z + 0Y, 7Z + 1Y, 6Z + 2Y, ..., or 0Z + 8Y first nearest neighbors (see Fig. 1(b) for representatives of the first coordination shell of the central X atom if Y and Z are randomly distributed on the 1a position of the $B2$ lattice).

The second sphere consists of 6 X atoms, and the third coordination sphere is built up by 12 X atoms. Thus, the

FIG. 1. (Color online) (a) Lattice of the $L2_1$ type structure and the corresponding first shell environments of the ^{59}Co nuclei, demonstrating that Co has only one environment in the first shell of the $L2_1$ structure, leading to the expectation of a single line in the NMR experiment. Partial substitution of Z by Z' leads to five different environments for the central ^{59}Co nucleus and thus to the expectation of five resonance lines. Please note, that the size and shape of the atoms shown in Fig. 1 is chosen only to allow a clear distinction between the different atoms and for the sake of clarity. (b) Lattice of the $B2$ type structure. A random distribution of the Y and Z atom leads to nine different environments corresponding to the expectation of nine resonance lines. A $B2$ type structure with a partial substitution of Z by Z' leads to 45 different environments.

second and the third shell are the same for the $L2_1$ and the $B2$ type structure, because they are not altered by the Y, Z intermixing. The fourth coordination sphere of the $L2_1$ structure consists of 12Y + 12Z atoms, while the Y, Z intermixing of the $B2$ type structure leads to 25 different fourth shell environments with varying numbers of Y and Z neighbors.

Implementation of the partial substitution of Z by Z' atoms within the $B2$ type structure will lead to a quaternary compound and to lines attributed to 0Y + 0Z + 8Z', ... 0Y + 8Z + 0Z', 2Y + 2Z + 4Z', ... 4Y + 4Z + 0Z', 4Y + 3Z + 1Z', 4Y + 2Z + 2Z', ..., 3Y + 5Z + 0Z', 3Y + 4Z + 1Z', ..., 7Y + 1Z + 0Z', 7Y + 0Z + 1Z', ..., or 8Y + 0Z + 0Z' first nearest

neighbors. This results in 45 possibilities to distribute n $Y + (n - k) Z + k Z'$ neighbors in the first shell of Co with $n_Y + m_Z + k_{Z'} = N = 8$ (see Fig. 1(b)).

IV. EXPECTED NMR SPECTRUM

The hyperfine interaction is the interaction of the nuclear magnetic moment with magnetic fields originating from the spin and orbital currents of the surrounding electrons. A prominent contribution to the hyperfine field is the transferred field, which depends on the neighboring atoms and their magnetic moments. Thus, the hyperfine field can be regarded as a probe of the local environment of the NMR active nucleus. Each first shell environment of the X atom, as introduced in Sec. III, will lead to a different hyperfine field and thus to a different resonance frequency.

A ternary, $L2_1$ ordered X_2YZ Heusler compound exhibits a single first shell environment (Sec. III), thus, only one sharp NMR resonance line should be observed (see Fig. 1(a)).

A quaternary compound $X_2YZ_{1-x}Z'_x$ with a partial substitution of the Z atom by Z' has five possible nearest neighbor environments of the central X atom (taking only the first shell into account) and will therefore have five possible hyperfine fields for the central X atom (see Fig. 1(a)).

The probability $P(n, x)$ for a particular surrounding of the form $n Z'$ atoms + $(4 - n) Z$ atoms in a certain shell of the central X atom is given by a binomial distribution which depends on the concentration x of the Z' atoms. The probability to find $n Z$ and $(4 - n) Z'$ on the $N = 4$ possible positions of the first neighbor shell of the X atom (assuming a $L2_1$ structure) is given by

$$P(n, x) = \frac{N!}{(N - n)!n!} (1 - x)^{N-n} x^n. \quad (1)$$

Note that Eq. (1) leads for $x = 0.5$ to symmetric distributions.

In the case of a $B2$ type structure, the random distribution of Y and Z is also described by a binomial distribution as given in Eq. (1), revealing the probability $P(n, x)$ for a particular environment of the form $n Y$ atoms + $(8 - n) Z$ atoms in the first shell of the central X atom. Here $N = 8$, which corresponds to the number of possible sites in the first shell of X , and x represents the ratio of the Y, Z intermixing. For a $B2$ type structure, this ratio corresponds to the site occupancy factor of the $1a$ position.

Assuming a $B2$ type structure with an additional random distribution of Z and Z' , the probability $P(n, k, m, x, y)$ for a particular surrounding of the form $n Y + (n - k) Z + k Z'$ atoms in a certain shell of the Co atom is now given by a multinomial distribution, which depends on the ratio x , corresponding to the ratio of the intermixing between the atoms on the $1a$ position, and on the ratio y , corresponding to the ratio of the partial substitution of Z by Z' ,

$$P(n, k, m, x, y) = \frac{N!}{n!(N - n - m)!m!} \times (1 - x)^{N-m-k} x^{m+k} y^k (1 - y)^{N-n-k}. \quad (2)$$

Note, that $n_Y + m_Z + k_{Z'} = N = 8$, correspond to the number of possible sites in the first shell of the X atom.

Figure 2 shows the probabilities calculated using Eq. (2). In order to demonstrate the effects of the random distribution of Z and Z' , lines corresponding to the same number of Y atoms have the same color. The main lines with the same number of Y atoms in the first shell have two sub-lines in the maximum for an odd number of Y atoms and one sub-line in the maximum for an even number of Y atoms. This leads also to the observation that main lines corresponding to odd number of Y atoms are broader and that the probability of the corresponding most prominent sub-line is lower. The sum of the areas of, i.e., the $5Y + (3 - k)Z + kZ'$ main line are the same as for the corresponding $3Y + (5 - k)Z + kZ'$ main lines. This follows from the symmetry of the binomial distribution with $x, y = 0.5$. Moreover, the number of sub-lines decreases with increasing resonance frequency of the main line.

In ferromagnetic materials, the most dominant contribution to the effective field experienced by a nucleus is the hyperfine field term. The hyperfine field, regarding the $3d$ metals, mainly consists of contributions from the Fermi-contact field.^{13,14} The Fermi-contact field is related to interactions with the on-site magnetic moments and the transferred contact field from neighboring atoms. Thus, pronounced differences in resonance frequencies hint on pronounced differences in the magnetic environment of the NMR active atom.

As an example, the spacing between adjacent lines in $L2_1$ ordered $Co_2Mn_{0.5}Fe_{0.5}Si$ is about 2 MHz.¹⁵ The origin of the observed line splitting is a random distribution of Mn and Fe in the third shell of the ^{55}Mn . The difference between the magnetic moments of Mn and Fe in $Co_2Mn_{0.5}Fe_{0.5}Si$ is quite small and thus the spacing between adjacent resonance lines is in the order of a few MHz.¹⁵

According to the considerations above, pronounced differences in resonance frequencies on the order of one magnitude larger than those caused by a distribution of magnetically similar atoms, hint on pronounced differences in the magnetic environment of the NMR active atom.¹⁶ Such an observation points to an intermixing of atoms with

FIG. 2. (Color online) The relative probabilities calculated using Eq. (2), corresponding to a $B2$ structure with a random distribution of the Z and Z' atoms. Note, that lines corresponding to the same number of Y atoms have the same color demonstrating that the sub-lines are related to the random distribution of Z and Z' .

FIG. 3. (Color online) The spin-echo intensity as a function of frequency for ^{59}Co in an as-cast sample of $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ (black dots) and the fit (gray line) resulting from Gaussian distributions (lines corresponding to the same number of Fe atoms have the same color corresponding to the fact the sub-lines are related to the random distribution of Al and Si). Moreover, there are five additional resonance lines, which correspond to the resonance lines of Co_2FeSi and Co_2FeAl apparent in the spectrum of $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ and to Co-Al and fcc Co (marked by arrows in Fig. 3). The resonance line at 177.5 ± 1.0 MHz could not be attributed to a particular ^{59}Co environment.

quite different magnetic moments. Regarding the Heusler compounds, the Y (in general a transition metal) and Z atoms (mostly a main group element) have this pronounced difference in magnetic moments. Thus, in case of a $B2$ type structure, one expects a frequency spacing of about one order of magnitude larger than for a random distribution of Z and Z' atoms.

Therefore, as a rule of thumb, in case both a $B2$ structure and a random distribution of Z , Z' are present, both main and sub-lines are expected. As mentioned above, the spacing between sub-lines related to the partial substitution of Z by Z' should be in the order of a few MHz, while the spacing between main lines, arising from the random distribution of Y and Z , Z' atoms, should be about one order of magnitude larger.

V. RESULTS AND DISCUSSION

A. Analysis of the ^{59}Co NMR spectrum of as-cast $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$

Figure 3 shows the ^{59}Co -NMR spectrum of $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ (as-cast sample). The measured NMR spectrum consists of four main lines with an underlying sub-structure and resonance signals originating from impurity phases.

In order to further analyze the spectrum and in particular to obtain the resonance frequencies of the main resonance signals, their spacings and their relative areas, the spectrum was fitted using a sum of Gaussian lines (gray line in Fig. 3). The widths of these Gaussian lines were restrained to be identical. This fit leads to an overall width of 13.3 ± 0.9 MHz for the main resonance lines of $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$. The resonance frequencies of these main lines and the corresponding hyperfine fields are listed in Table I.

The most prominent resonance line is found at 161.1 ± 0.1 MHz. This resonance frequency roughly corresponds to the mean of the resonance frequencies of the most prominent resonance lines of the Heusler compounds Co_2FeAl (about 192.3 MHz, Ref. 17) and Co_2FeSi (about 138.7 MHz). Thus, the most pronounced resonance frequency reflects the substitution of 50% Al with 50% Si.

The mean spacing between adjacent sub-lines is about 7.0 ± 0.1 MHz, corresponding to a difference in hyperfine field of 0.7 T, for the as-cast sample. The linewidth of the sub-lines is found to be 5.8 ± 0.5 MHz.

According to the rule of thumb, as explained in Sec. III, and taking the rather similar on-site magnetic moments of Al and Si into consideration,¹⁰ a partial substitution of Al by Si should lead to a rather small change in the hyperfine field at the ^{59}Co nucleus and consequently to a small spacing between the corresponding resonance lines. Thus, the splitting into the sub-lines might be related to the distribution of the Al and Si atoms. Regarding the resonance frequencies of Co_2FeSi and Co_2FeAl , apparently the resonance lines of the low frequency site correspond to ^{59}Co nuclei with more Si atoms in the first shell, while the Fe-rich environments are on the high frequency site of the corresponding main line. However, the mean spacing between adjacent main lines (neglecting the underlying sub-structure) is ~ 31 MHz, corresponding to a difference in hyperfine field of 3 T (see Fig. 3 and Table I for details), pointing to significant differences in the magnetic environments of the corresponding ^{59}Co nuclei (as explained in Sec. III).

In the following, the discussion of the origin of the sub-lines attributed to the random distribution of Al and Si will be postponed to a later section, and we will start with the discussion of the origin of the main lines.

The observed spacing of the main resonance lines in $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ is comparable to the spacing observed for adjacent main lines measured by NMR for Co_2FeAl with an intermixing of the Fe (corresponding to the Y atoms on the Wyckoff $4b$ positions) and Al atoms (corresponding to the Z atoms on the Wyckoff $4a$ positions).^{17,18} The quite large

TABLE I. Main resonance lines obtained by ^{59}Co NMR, corresponding distribution of Fe and $(8-k)Z+kZ'$ in the first coordination shell of the ^{59}Co nuclei, the resonance frequencies, and the corresponding hyperfine fields H_{hf} .

Line	Corresponding atom distribution in first shell	Frequency (MHz)	Spacing (MHz)	Hyperfine field (T)	Spacing (T)
1	$3\text{Fe} + (5-k)Z + kZ'$	130.3 ± 0.4	~ 31	13.0 ± 0.1	~ 3
2	$4\text{Fe} + (4-k)Z + kZ'$	161.1 ± 0.1	~ 31	16.0 ± 0.1	~ 3
3	$5\text{Fe} + (3-k)Z + kZ'$	191.8 ± 0.2	~ 31	19.1 ± 0.1	~ 3
4	$6\text{Fe} + (2-k)Z + kZ'$	223.1 ± 0.4		22.2 ± 0.1	

spacing of ~ 27 MHz (corresponding to a hyperfine field of 3 T) arises from the rather large differences in the magnetic environment of the ^{59}Co nuclei, caused by an intermixing of Fe ($2.75 \mu_B$, Ref. 19) and Al ($\sim 0 \mu_B$, Ref. 19) in Co_2FeAl . Moreover, Niculescu *et al.*²⁰ reported that Fe-rich environments in Co_2FeSi (without Al) lead to additional resonance frequencies above the main line with a spacing of roughly 30 MHz (corresponding to a hyperfine field of 3 T). This is consistent with the assignment of Fe-rich and Si-poor environments reported for off-stoichiometric Co_2FeSi thin films.^{16,21} In conclusion, the main lines in our spectra have to be assigned to environments with different numbers of Fe next neighbors.

This interpretation is also supported by the following arguments: If we tentatively would assume that the main lines arise from a random distribution of Al and Si (see also Sec. IV), then, the observed main lines must be assigned to different numbers of Al and Si next neighbors. Now, the first main line (130 MHz) should correspond to $3\text{Si} + 1\text{Al}$ neighbors (calculated probability of 27%, according to Eq. (1)), the second (161 MHz) to $2\text{Si} + 2\text{Al}$ (probability of 40%), the third (192 MHz) to $1\text{Si} + 3\text{Al}$ (probability of 27%), and the fourth (223 MHz) to $0\text{Si} + 4\text{Al}$ (probability of 7%). It is immediately apparent that the calculated probabilities do not fit to the experimentally found relative areas of the main resonance lines. The most prominent line in the experiment yields, e.g., a relative area of 60%, the third 20%. This definitively excludes an assignment of the main lines to a random distribution of Al and Si. If there would be only a random distribution of Al and Si present, the calculated probabilities should fit the experimentally found relative areas.

Moreover, by tentatively assuming a random Al/Si distribution, the line with $0\text{Si} + 4\text{Al}$ next neighbors (corresponding to the first shell environment of Co_2FeAl) should be identified with the resonance line experimentally found at 223 MHz. This is roughly 30 MHz higher than the corresponding line of pure Co_2FeAl (which intrinsically has no Si next neighbours). According to the literature, Si as a next neighbor lowers the resonance frequency and, thus, can also not explain why the line at 223 MHz (assumable corresponding to $0\text{Si} + 4\text{Al}$ next neighbors) should have a higher resonance frequency than pure Co_2FeAl . As a first conclusion, the assumption of a random distribution of Al and Si inevitably leads to the problem of properly assigning the observed hyperfine fields to all environments.

The main resonance line at 161 MHz, attributed to the resonance line of $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ with the $L2_1$ type structure, consists of five sub-lines. Thus, the resonance line of ordered $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ exhibits exactly the number of sub-lines expected for a random distribution of Al and Si. Moreover, the low frequency sub-lines of this main line correspond to the Si-rich environments with 4 Fe next neighbors and the high frequency sub-lines correspond to the Al-rich environments with 4 Fe next neighbors (blue sub-lines in Fig. 3). The resonance frequencies of these Si-rich environments are higher than for pure Co_2FeSi , due to the transferred hyperfine field contribution from atoms in higher shells (Al increases the frequency also in higher shells). A similar effect explains why the Al-rich environments with 4 Fe neighbors also have a lower frequency than the pure

Co_2FeAl . Taking higher shells into account, there is a certain (small) probability to observe environments with the same first and higher shell environment as in pure Co_2FeAl .

In conclusion, the observation of four main lines and an underlying sub-structure cannot be explained by Co nuclei experiencing only the $L2_1$ environment, even if a random distribution of Al and Si is assumed. In line with the interpretation of the additional main lines in Co_2FeAl (Refs. 18 and 21) and Co_2FeSi ,^{16,20} the observation of the four main resonance lines in $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ might point to an intermixing of Fe with the $Z + Z'$ atoms and therefore to contributions from the $B2$ type structure. From a crystallographic point of view, the entire random distribution of Y and Z atoms on the Wyckoff $1a$ position (the former $4a$ and $4b$ positions of the $L2_1$ structure, space group $Fm\bar{3}m$) of the $Pm\bar{3}m$ space group is the basic requirement of the $B2$ structure, while an entire preferential order would lead to a different structure type and a different space group.

Comparing the probabilities calculated by using Eq. (2) with the experimental results, the existence of $B2$ type contributions with an additional random distribution of Al and Si in $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ is confirmed. Moreover, the most prominent main line found in the NMR spectrum reflects the partial substitution of Al by about 50% Si, corresponding to Co nuclei with $4\text{Fe} + (4 - k)\text{Al} + k\text{Si}$ next neighbors. This line corresponds to the most prominent line predicted by the multinomial distribution calculated using Eq. (2). However, the overall probability of the lines with $4\text{Fe} + (4 - k)\text{Al} + k\text{Si}$ neighbors is significantly larger (about 137%) than the calculated probability according to a binomial distribution with entirely random distribution of Fe and Al and Si. This means that the distribution of these atoms is not entirely random, but also has contributions of ^{59}Co nuclei with a preferential $4\text{Fe} + (4 - k)\text{Al} + k\text{Si}$ first shell environment. In particular, this preferentially enhanced resonance line corresponds to the environment of $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ with $L2_1$ type structure assuming a compound with a random distribution of Al and Si. In conclusion, $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ is measured to be of $B2$ type structure with contributions of the $L2_1$ type structure.

In order to determine the corresponding ordering parameters of the $B2$ and $L2_1$ type structure, a multinomial distribution (as introduced in Eq. (2)) has to be expressed as the sum of $B2$ and $L2_1$ contributions, leading to

$$P(n, x, b_{B2}, l_{L2_1}) = b_{B2} \cdot \frac{N!}{n!(N - n - m)!m!} \times (1 - x)^{N-m-k} x^{m+k} y^k (1 - y)^{N-n-k} + l_{L2_1} \cdot \frac{L!}{(L - l)!} (1 - q)^{L-l} q^l \delta_{n,4} \quad (3)$$

$$\text{with } \delta_{n,4} \begin{cases} 1, & \text{if } n = 4 \\ 0, & \text{if } n \neq 4 \end{cases} \quad (3a)$$

The first term represents the $B2$ contributions with a random distribution of Al and Si (an intermixing of Fe, Al, and Si on the $1a$ position). The probability $P(n, k, m, x, y)$ for a particular surrounding of the form $nY + (n - k)Z + kZ'$ in a certain shell of the Co atom is then given by the first term of the

binomial distribution (in Eq. (3)). Moreover, the $B2$ contribution depends on the ratio x , corresponding to the ratio of the intermixing between the atoms on the $1a$ position, and on the ratio y , corresponding to the ratio of the partial substitution of Z by Z' .

The second term accounts for the $L2_1$ contributions. However, the random distribution of Al and Si, which is also apparent for the $L2_1$ structural phase, also has to be represented by a binomial distribution with $L=4$, corresponding to the number of possible sites related to the $4a$ position in the first shell of the ^{59}Co nuclei assuming an $L2_1$ structure. Thus, it is presumed that $0 \leq l \leq 4$ in order to take the random distribution of Al and Si into account. For a $L2_1$ type structure one expects the observation of 5 (more or less resolved) lines due to the random distribution of Al and Si (see Fig. 1), which results in a probability $P(L2_1) = 1$ for the observation of these particular environments in the $L2_1$ structure.

The ordering parameters b_{B2} , l_{L2_1} represent the relative contributions for ^{59}Co nuclei with a $B2$ first shell and a $L2_1$ first shell environment, respectively. Note, that the overall probability has to sum up to 100% and, thus $b_{B2} + l_{L2_1} = 1$.

Figure 4 shows the relative areas as obtained by a fit with Gaussians and the relative probabilities according to Eq. (3), taking both $B2$ and $L2_1$ contributions into account. Note, that the available frequency range in the current experimental setup excludes the observation of the $n=0, 1, 2$ environments, however, the probability to observe these particular environments is only about 10% and the overall probability was corrected for this. Furthermore, the probability for the $n=7, 8$ environments is too low to be observed in the experiment. The matching between the relative areas and the calculated probabilities was optimized by varying x , y , q , b_{B2} , and l_{L2_1} (monitored by a least square method) leading to the optimum values $x = 0.47 \pm 0.01$, $y = 0.49 \pm 0.01$, $q = 0.50 \pm 0.01$, $b_{B2} = 0.62$, and $l_{L2_1} = 0.38$. The deviation between the relative area of the resonance signal and the

calculated probability for the $4\text{Fe} + (4 - k)\text{Al} + k\text{Si}$ environments leads to a very good agreement between the experimentally found relative areas and the relative probabilities calculated with Eq. (3) by taking additional $L2_1$ contributions into account. The ordering parameter $l_{L2_1} = 0.38$ reveals a contribution of 38% of the $L2_1$ structure.

However, completely separated regions of $B2$ ordering within an $L2_1$ matrix are unlikely. The multinomial random atom model rather reveals, that ^{59}Co nuclei are existing with a first shell environment of the $B2$ type order, corresponding to lower and higher numbers of Fe next neighbors in the first shell, and ^{59}Co nuclei with a first shell environment of the $L2_1$ type order. These varying environments are present not only in the first shell, but also in higher shells. That is one reason, why e.g., the resonance frequency of the sub-line with $4\text{Fe} + 4\text{Si}$ next neighbors (149 MHz) is different from the resonance frequency of pure Co_2FeSi (138 MHz). The Al atoms in higher shells will lead to a frequency shift toward higher frequencies.

The observation of $B2$ contributions in the as-cast sample is not unexpected due to the rapid cooling usually done after arc-melting. The $B2$ phase remains metastable in the sample, leading to the observation of both $B2$ and $L2_1$ type ordering.

However, a fit with the expected 18 lines (in the applicable frequency range) with a constant sub-line spacing of about 7 MHz was not sufficient to explain all observed resonance lines. At certain frequencies (like, e.g., at 192 MHz in the as-cast sample spectrum), a prominent resonance line is observed in the spectrum. These five additional resonance lines apparent in the spectrum of the as-cast sample (marked by arrows in Fig. 3) always showed a sub-line spacing different from the 7 MHz observed for the resonance lines attributed to the different structural contributions of $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$. The fits were significantly improved by one order of magnitude by including the resonance lines attributed to contributions different from $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ (using χ^2 as a measure of the fit quality). The frequencies of the two additional resonance lines found at 138.3 MHz and at 192.8 MHz (marked by arrows in Fig. 3) correspond to the resonance lines of Co_2FeSi (about 0.5% of the overall area of the spectrum) and Co_2FeAl (about 1.6% of the overall area of the spectrum), respectively. The observation of these resonance lines points to ^{59}Co nuclei in the as-cast sample which have the same first and higher shell environments as the ternary, parental compounds. Also, small amounts of CoAl (Ref. 22) (1%) and fcc Co (Ref. 23) (1.2%) are observed at 208 ± 1 MHz and 213 ± 1 MHz, respectively. A fifth additional resonance line is observed at 177.5 ± 1 MHz and could up to now not be attributed to a particular Co environment (about 1%). Thus, in total, about 5% contributions of foreign phases are identified. This small amount of additional phases might be very difficult to detect with other methods.

In summary, the $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ as-cast sample consists of a $B2$ structure with about 38% contributions of a $L2_1$ type structure, and the random distribution of Al and Si is apparent in both structural phases. The as-cast sample shows small amounts of the ternary parental alloys, as well as of CoAl and fcc Co .

FIG. 4. (Color online) (a) Comparison of the relative areas as obtained by a fit with Gaussians and the relative probabilities according to Eq. (3), corresponding to a $B2$ structure with $L2_1$ contributions with a random distribution of Al and Si in both structural contributions and (b) the difference between both. The matching between the relative areas and the calculated probabilities was optimized by adaption of the fractions $x = 0.47 \pm 0.01$, $y = 0.49 \pm 0.01$, $q = 0.50 \pm 0.01$, $b_{B2} = 0.62$, and $l_{L2_1} = 0.38$.

FIG. 5. (Color online) The spin-echo intensity as a function of frequency for ^{59}Co in an at 873 K annealed sample of $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ (black dots) and the fit (gray line) resulting from Gaussian distributions (lines corresponding to the same number of Fe atoms have the same color corresponding to the fact the sub-lines are related to the random distribution of Al and Si). Moreover, there are five additional resonance lines, which correspond to the resonance lines of Co_2FeSi and Co_2FeAl apparent in the spectrum of $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ and to CoAl and fcc Co (marked by arrows in Fig. 3). The resonance line at 177.5 ± 1.0 MHz could not be attributed to a particular ^{59}Co environment. The inset shows a comparison between the annealed (black squares) and the as-cast sample (red dots). The spin-echo intensity was normalized in order to compare both spectra.

B. Analysis of the ^{59}Co NMR spectrum of annealed $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$

Figure 5 shows a comparison of the ^{59}Co NMR spectra of $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ annealed at 873 K and an as-cast sample as discussed in the previous section (see also Table II). The identical sample was determined by Balke *et al.*¹⁰ to be a single phase material having the $L2_1$ structure for this annealing temperature (in particular seen in Fig. 3 of Ref. 10).

The same fitting procedure as used for the as-cast sample was applied to the annealed sample. In line with the results of the as-cast sample, a significantly improved fit required the implementation of additional resonance lines. The observation of the four main lines clearly confirms $B2$ contributions also for the annealed sample. The ratio between the $B2$ and $L2_1$ contributions changes by annealing, leading to more $L2_1$ contributions. This is already apparent by a visual inspection of the two spectra, because the $L2_1$ resonance line of the annealed sample is distinctly sharper (see Table II), and because the relative areas of the resonance lines attributed to the $\text{Fe} + (\text{Al}, \text{Si})$ intermixing ($B2$ type contributions) are reduced. The resonance frequency of the sub-lines as well as the spacing between adjacent sub-lines is not significantly changed by the annealing process. This is reasonable, as the sub-structure related to the random distribution of Al and Si is already apparent in the sample before the annealing process. The higher ratio of the $L2_1$ type structure contribution indicates the influence of the annealing process. However, $B2$ contributions (as well as contributions of foreign phases) are also apparent in the annealed sample indicating that the annealing process was not fully successful.

In addition, the fact that the intensities of the three main lines decrease after an appropriate annealing process, also confirms the assignment of the main lines to $B2$ contribu-

TABLE II. Comparison of the as-cast sample with the annealed sample.

	As-cast sample	Annealed sample
Mean spacing main lines (MHz)	~ 31	~ 32
Width of main lines (MHz)	13.3 ± 0.5	8.6 ± 0.5
Mean spacing sub-lines (MHz)	7.0 ± 1	7.3 ± 0.9
Width sub-lines (MHz)	5.8 ± 0.5	5.3 ± 0.1
$L2_1$ contribution	38%	59%

tions. If the main lines would be caused by a random distribution of Al and Si, one would expect that the main lines would not be significantly effected by an annealing at this particular temperature. Thus, in line with the arguments above, the decrease of the intensity of the main lines, in addition to the smaller linewidth (due to a lower degree of $B2$ order also in higher shells), is further proof that the main lines have to be associated with a $B2$ ordering.

Furthermore, the two additional resonance lines, corresponding to the resonance lines of Co_2FeSi and Co_2FeAl , are still present after annealing, as well as the contributions of CoAl and fcc Co , and also the contribution at 177.5 ± 1.0 MHz (see Fig. 5).

According to band structure calculations, the degree of spin polarization is conserved for Co_2FeAl (Refs. 19 and 24) in the $B2$ type structure, but decreased for Co_2FeSi .²⁵ The band structure calculation found in Ref. 10 reports a very stable half-metallicity of $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$. The calculations were based on a supercell assuming a preferential distribution of Al and Si (see Ref. 9 for details). A band structure calculation including a $B2$ type structure and a random distribution of Al and Si would prove, whether a high spin polarization and the position of the gap predicted for $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ would be conserved under this condition.

VI. SUMMARY

In summary, the ^{59}Co NMR measurements confirmed the expected random distribution of Al and Si in $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$. This random distribution is attributed to the appearance of a sub-structure in the NMR spectra. However, this random distribution is not only related to a $L2_1$ structured but also to a $B2$ structured phase. This $B2$ contribution leads to the observation of four main resonance lines. The main structural contribution of $\text{Co}_2\text{FeAl}_{0.5}\text{Si}_{0.5}$ as-cast bulk samples is of $B2$ type with 38% $L2_1$ contributions. An appropriate annealing process enhances the $L2_1$ contributions to 59%.

ACKNOWLEDGMENTS

The authors acknowledge sample preparation by C. G. F. Blum and B. Balke (both Johannes Gutenberg-Universität, Mainz). Moreover, the authors thank G. Malinowski for discussion as well as J. J. P. A. W. Noijen and G. Baselmans for technical support. S.W. gratefully acknowledges funding by DFG in project No. WU595/1-1 and by the Emmy-Noether program (Grant No. WU595/3-1).

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