Mn-55 NMR study of quaternary half-metallic ferromagnetic Co2Mn1-xFexSi Heusler compounds


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In this work, the $^{55}$Mn spin-echo nuclear magnetic resonance technique is used to systematically analyze the complete substitutional series $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ in terms of the resonance frequencies of the satellite structure and the corresponding hyperfine fields of the $^{55}$Mn nuclei. The frequency spacing between satellite lines is constant within a compound, but decreases with increasing Fe concentration $x$, which originates in changes in the band structure. These changes are also responsible for the altered resonance frequencies observed for the same third shell environment but corresponding to a different overall Fe concentration $x$. All modifications in the hyperfine field upon substitution of Mn by Fe can be uniquely assigned to an entirely random distribution of Mn and Fe limited to only one (4$b$) out of four fcc sublattices constituting the $L2_1$ Heusler structure, demonstrating that the complete substitutional series $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ is crystallographically very well defined. This very high degree of order sets the stage for the observation of stable half-metallic ferromagnetism which is typically very sensitive to the structural order.

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I. INTRODUCTION

Half-metallic ferromagnets having a high stability of the minority band gap and, thus, a robust half-metallic behavior, are favored for spintronic applications.\textsuperscript{1,2} If the Fermi energy is close to one of the edges, the band gap may easily be affected by disorder or by quasiparticle excitations.\textsuperscript{1,2} Therefore, compounds with the Fermi energy located in the middle of the band gap are highly desirable.\textsuperscript{1,2} A tunnel magnetoresistance device showing 832\% TMR at 2 K and 386\% at room temperature has been realized using the quaternary Heusler compound $\text{Co}_2\text{FeAl}_0\text{Si}_{0.5}$ as one example of such a robust half-metallic ferromagnet.\textsuperscript{3} In addition, Shan \textit{et al.} reported that this material exhibits half-metallic ferromagnetism even at room temperature.\textsuperscript{4} Members of the substitutional series $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ with $x \approx 0.5$ are also predicted to exhibit this particular stable half-metallic behavior.\textsuperscript{5} They belong to the class of $X_2YZ$ Heusler compounds,\textsuperscript{6} crystallizing in the $L2_1$ structure with the related space group $\text{Fm}$5$\overline{m}$.\textsuperscript{7}

Several types of disorder were identified in Heusler compounds,\textsuperscript{3} which have been also experimentally observed (see, e.g., Ref. 8 and references therein). The ordering in these different structure types have a high impact on the spin polarization, as some types of antisite disorder destroy half-metallic ferromagnetism,\textsuperscript{9–12} requesting thorough structural characterization.

The structure of the complete substitutional series $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ was studied and verified to be $L2_1$ by combining several techniques such as x-ray diffraction, Möbbauer spectroscopy, extended x-ray absorption fine-structure measurements, high- and low-temperature magnetometry, and differential scanning calorimetry.\textsuperscript{1,13,14} In addition to the predicted high spin polarization and high degree of order, the $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ series also offers very high Curie temperatures, namely 1100 K [Co$_2$FeSi (Ref. 13)] and 985 K [Co$_2$MnSi (Ref. 1)].

From a crystallographic point of view, the $L2_1$ structure type requires a random distribution of the Mn and Fe atoms on the 4\textit{b} Wyckhoff position in the case of the quaternary compounds, whereas a complete preferential ordering would lead to a different structure type, symmetry, and space group. Nuclear magnetic resonance (NMR) spectroscopy is able to distinguish between a preferential ordering and a random distribution of Mn and Fe in $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$.\textsuperscript{15–17} The NMR frequencies are strongly dependent on the local environment of the probed nuclei ($^{55}$Mn) which provides the possibility to resolve the occupation and local hyperfine fields of the nearest coordination shells of this atoms.\textsuperscript{15,18–21} In some cases higher shell effects are visible as well.

In this paper, NMR was used to investigate the local environment of the complete substitutional series $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ and in particular to analyze the impact of the partial substitution on the $^{55}$Mn hyperfine magnetic field (for experimental details see Ref. 22). By comparison of different structural models, the origin of the line splitting is identified as a random distribution of Mn and Fe in the third and higher shells. It is shown that the frequency spacing between adjacent resonance lines decreases with increasing Fe concentration $x$. This points to changes in the transferred hyperfine fields with increasing Fe concentration $x$, similarly to the observation of Wójcik \textit{et al.} for Co$_2$FeAl$_{1-x}$Si$_x$.\textsuperscript{23} The band-structure calculations,\textsuperscript{1} predicting a very stable half-metallicity of the compounds with $x \approx 0.5$ were performed using a supercell with a preferential distribution of Fe and Mn. Thus, it might be quite relevant to recalculate the band structure of Co$_2$Mn$_{1-x}$Fe$_x$Si including the experimentally verified random distribution of Mn and Fe, and to check whether the minority band gap and the half-metallicity is conserved. The high crystallographic order of all members...
of the substitutional series, demonstrated by the $^{55}$Mn NMR results, sets stage for the half-metallic character and the high degree of spin polarization of Co$_2$Mn$_{1-x}$Fe$_x$Si and illustrates that in particular the Co$_2$Mn$_{1-x}$Fe$_x$Si compounds with $x \approx 0.5$ may be ideal candidates for spintronic applications.

II. RESULTS AND DISCUSSION

A. NMR spectra of the Co$_2$Mn$_{1-x}$Fe$_x$Si substitutional series

The NMR experiments were performed on pieces of polycrystalline samples in an automated, coherent, phase sensitive spin-echo spectrometer at temperature $T = 4.2$ K, and at zero external magnetic field. All NMR spectra were corrected for the magnetic enhancement factor as well as for the $\nu^{-2}$ dependence. For experimental details see Ref. 22.

Figure 1 shows the $^{55}$Mn NMR spectra of all members of the substitutional series together with the Heusler crystal lattice (L$\text{\textsubscript{2}}$$_1$-type structure) and the corresponding Wyckoff positions of the X, Y, and Z atoms. Note that all spectra are scaled in order to better represent the increasing Fe content. Apparently, the spectra shift to higher resonance frequencies with increasing Fe content $x$. As can be seen, all spectra exhibit a splitting into resonance sublines (satellite lines). For further analysis the observed lines of all spectra were fitted using a sum of Gaussian lines (represented in Fig. 2 by thick solid lines). Note that the labels of the individual lines in Fig. 2 represent the Fe and Mn occupations in the third-neighbor shell of the $^{55}$Mn nuclei, which determine the resonance frequency for a given surrounding, as will be discussed in Sec. II C. The width of these Gaussian lines were constrained to be identical within each compound. Figure 2 shows the $^{55}$Mn spectra of Co$_2$Mn$_{0.1}$Fe$_{0.9}$Si (a), Co$_2$Mn$_{0.3}$Fe$_{0.7}$Si (b), Co$_2$Mn$_{0.7}$Fe$_{0.3}$Si (c), and Co$_2$Mn$_{0.9}$Fe$_{0.1}$Si (d) as representatives of the Co$_2$Mn$_{1-x}$Fe$_x$Si substitutional series. It has been found that the frequency spacing between the satellites, within some experimental uncertainty, remains constant for each spectrum. However, this frequency spacing shows a pronounced dependence on the Fe concentration. The results of the analysis, such as mean spacing and mean satellite linewidth for a particular Fe concentration, are given in Table I.

A comparison of the satellite linewidths of the complete substitutional series (see also Ref. 16) reveals that the linewidth $\Gamma$ first increases with increasing Fe concentration $x$ but
table I. Mean spacing between adjacent lines, the mean width of the lines in the spectra of Co₂Mnₓ₋₁FeₓSi and the mean absolute |⟨δ⟩| values calculated using Eq. (5).

| x   | Mean spacing (MHz) | Mean width (MHz) | Mean |⟨δ⟩| (×10⁶ A / m₂πγ | |
|-----|---------------------|------------------|------|----------------------------|
| 0.1 | 3.05 ± 0.08         | 1.78 ± 0.15      | 0.64 ± 0.02 |
| 0.2 | 2.93 ± 0.11         | 1.91 ± 0.08      | 0.64 ± 0.03 |
| 0.3 | 2.70 ± 0.10         | 1.99 ± 0.35      | 0.61 ± 0.02 |
| 0.4 | 2.66 ± 0.08         | 2.11 ± 0.06      | 0.62 ± 0.02 |
| 0.5 | 2.35 ± 0.07         | 2.19 ± 0.27      | 0.58 ± 0.02 |
| 0.6 | 2.19 ± 0.08         | 2.05 ± 1.35      | 0.55 ± 0.02 |
| 0.7 | 2.07 ± 0.20         | 1.95 ± 0.54      | 0.55 ± 0.02 |
| 0.8 | 1.59 ± 0.09         | 1.36 ± 0.20      | 0.43 ± 0.02 |
| 0.9 | 1.60 ± 0.09         | 1.28 ± 0.27      | 0.42 ± 0.02 |

eventually decreases after reaching a maximum (around 2 MHz at medium Fe concentration compounds). Interestingly, the linewidth of the Fe-rich compounds is even smaller than the linewidth of the Mn-rich compounds (see Sec. II H).

B. Contributions to the hyperfine field

The most dominant contribution to the effective field experienced by a nucleus in ferromagnetic materials is the hyperfine field term which for 3d metals mainly consists of contributions from the Fermi-contact field. The Fermi-contact field is related to interactions of electrons with the on-site magnetic moments mediated via the hyperfine coupling constants. Besides the contributions from the on-site magnetic moments, a significant contribution is the transferred contact field from the neighboring atoms which emerges from the polarization of the conduction s electrons by the magnetic moments of the surrounding atoms. Bearing this in mind, pronounced differences in resonance frequencies consequently hint to pronounced differences in the magnetic environment of the NMR active atom. Apart from that, this term makes the hyperfine field sensitive to changes in the local crystallographic environment. Please note that the coupling constants for the core and the transferred contributions to the contact field are related to the electronic structure of a system, which allows one to monitor changes in the electronic structure at least qualitatively by studying the evolution of the hyperfine fields, e.g., within a substitution series. Therefore, the measurement of the hyperfine field gives the possibility to study the local magnetic, electronic, and structural surroundings of the NMR active atom.

C. Origin of the hyperfine field splitting

It is well known that antideuterium, yielding different types of structure (A₂, B₂, or DO₃), affects the local hyperfine fields in clearly distinguishable ways. For example, the A₂ type order yields a single, but very broad NMR line, which consists of many unresolved resonance lines corresponding to a large number of possibilities to distribute X, Y, and Z atoms on the 1a position of the A₂ lattice. In the case of A₂ ordered Co₂FeAl the ⁵⁹Co NMR linewidth amounts to a value of about ∼100 MHz (∼10 T). The B₂-type order (intermixing of Y and Z atoms) leads to a splitting of the resonance line to a set of sublines with a rather large spacing, due to pronounced differences in the magnetic moments between a transition metal and a main group element. In the case of Co₂Mn the spacing, measured on ⁵⁵Mn nuclei, is about ∼50 MHz (∼5 T). Similarly, in the case of Co₂FeAl, Y/Z mixing (B₂-type order) leads to the splitting of the ⁵⁹Co lines with a spacing of about ∼30 MHz (∼3 T). In addition, B₂-type order in Co₂Mnₓ₋₁FeₓAl yields only seven Mn/Fe sites with nonequivalent local hyperfine field, as it is shown in Ref. 3. The DO₃-type order (exchange of X and Y atoms) leads to a reduction of the hyperfine field at the Y atoms yielding a splitting into nine sublines.

As can be seen in Fig. 2, the number of well identified lines for Co₂Mnₓ₋₁FeₓSi continuously changes from 6 to 11 and then back to 7 with increasing Fe content x. This fact together with experimentally observed line spacing (see Table I) rules out A₂, B₂, and DO₃ types of order in Co₂Mnₓ₋₁FeₓSi. In addition, the ⁵⁹Co NMR measurements performed on the same samples support the absence of A₂, B₂, and DO₃ types of order (⁵⁹Co NMR data were not included in this work).

Consequently, the line splitting is attributed to the L₂₁ structure with a random distribution of Mn and Fe on the 4b position, leading to the existence of ⁵⁵Mn atoms with a varying number of Fe neighbors. Every satellite line in the ⁵⁵Mn NMR spectra is attributed to a different number of Fe next neighbors in the third shell of the ⁵⁵Mn nuclei. Assuming that Fe randomly substitutes for Mn, the probability to find a certain surrounding of the ⁵⁵Mn nuclei is given by the binomial distribution, represented by Eq. (1) (random atom model). In the present case, the probability to find n Mn and (12-n) Fe on the N = 12 positions of the third coordination shell of the ⁵⁵Mn nuclei in the L₂₁ structure in a particular compound with the overall Fe concentration x is given by

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

D. Comparison of the binomial random atom model with the experimental data

In order to further confirm the random distribution of Mn and Fe for the complete substitutional series and to determine the real Fe concentration x, the relative areas of the resonance lines found experimentally are compared to the relative probabilities obtained by Eq. (1) (see Fig. 3). The determination of the real Fe concentration x was done by fitting the probability predicted by a binomial distribution [Eq. (1)] to the experimental data, having the Fe concentration x as a fit parameter. This optimization process was monitored by the least-square method (see Refs. 15 and 21 for details). For the comparison of the measured Fe concentration x with the nominal see Ref. 37.

The comparison of the experimental results with the binomial distribution curves explains the observation of less than 13 lines in all ⁵⁵Mn spectra, as the probabilities for some particular surroundings (e.g., 6 Fe + 6 Mn, 7 Fe + 5 Mn, etc., for Co₂Mn₀ₓFe₀ₓSi, Fig. 2) are too low to be observed in the NMR experiment. This also explains the increase in the number of lines with increasing Fe concentration x and the decrease to 7 lines for Co₂Mn₀ₓFe₀ₓSi after a maximum of
The probabilities to observe a particular neighboring environment as explained in the following. The full symbols represent the results obtained by fitting the experimental data with Gaussian lines, while the open symbols represent the probabilities as calculated using a binomial distribution of Fe on the 4b position. The lines are drawn to guide the eye.

11 lines (Co₂Mn₀.₃Fe₀.₅Si). The shape of all experimentally obtained distribution curves (Fig. 3, full symbols) follows the calculated binomial distribution (Fig. 3, open symbols). This confirms the predominantly random distribution of Fe and Mn on the 4b position for the complete substitutional series. Smaller deviations of the experimental data from the binomial distribution model are observed for the Fe-rich compounds than for the Co₂FeSi. On the other hand, all samples represent almost ideal intrinsic property of these compositions. This observation may be related to the properties of a particular sample but is an intrinsic property of these compositions. This supports the approximation that the local field Hₓ₊₀(ₐₓ) experienced by the 0 atom, the contribution of the contact hyperfine field term may be written as hₓ₊₀(ₐₓ), where mₓ₊₀(ₐₓ) is the moment of the jth atom I = X, Y, or Z in the ith shell. For the X₂Y₁₋ₓZₓ compound this relates to

\[ H(Y₀) = H₀(Y) + 8h₁m(X) + 6h₂m(Z) + h₃[(12 - n)m(Y) + nm(Y')] + 24h₄m(X) + 8h₅m(Z) + h₆[(6 - n)m(Y) + nm(Y')] + \cdots \]  

where the indices are for the ith shell. In a simple model each contact hyperfine field term may be written as hₓ₊₀(ₐₓ), where mₓ₊₀(ₐₓ) is the moment of the jth atom I = X, Y, or Z in the ith shell. For the X₂Y₁₋ₓZₓ compound this relates to

\[ H(Y₀) = H₀(Y) + 8h₁m(X) + 6h₂m(Z) + h₃[(12 - n)m(Y) + nm(Y')] + 24h₄m(X) + 8h₅m(Z) + h₆[(6 - n)m(Y) + nm(Y')] + \cdots \]  

The terms with h₂ and h₃ are negligible as the Z element does not add to the magnetic moment. In order to focus on the analysis of the most important contributions to the hyperfine field H(Y₀) experienced by the Y₀ atom, the contribution of coordination shells higher than the third shell can also be neglected in the first approximation, which simplifies Eq. (3) and leads to Eq. (4):

\[ H(Y₀) = H₀(Y) + 8h₁m(X) + h₃[(12 - n)m(Y) + nm(Y')] \]  

According to Eq. (4), one expects a constant splitting of the resonance lines for a particular compound if one assumes that the magnetic moments and H₀(Y) are not changed by an environment alteration.

In line with this simple model, Fig. 4 demonstrates that the spacing between adjacent resonance lines can be regarded as nearly constant within each compound, with some experimental uncertainty (see spacing between vertical lines of symbols with each line corresponding to a certain compound). This supports the approximation that the local field Hₓ₊₀(Y) and the magnetic moments of Co, Mn, and Fe are not changed by the partial substitution of Mn and Fe within a compound. In addition, the dependencies of the resonance frequencies assigned to a particular number of Fe neighbors for all spectra follow reasonably well the linear fits depicted as straight solid lines in Fig. 4. This linear dependence on the Fe concentration

**E. Influence of the partial substitution of Mn by Fe on the hyperfine field**

The probabilities to observe a particular neighboring environment can be directly compared to the intensities of a spin-echo NMR measurement. The corresponding resonance frequencies are related to the hyperfine fields of the active atom in this certain environment as explained in the following.

The hyperfine field H(Y₀) experienced by the Y₀ atom will depend on a particular environment and one expects that the effective hyperfine field at the atom Y₀ is composed of the on-site hyperfine field H₀(Y₀) and the transferred hyperfine fields emerging from the magnetic moments of the surrounding atoms:26

\[ H(Y₀) = H₀ + H₁ + H₂ + H₃ + \cdots = \sum Hᵢ \]  

where the indices are for the ith shell. In a simple model each contact hyperfine field term may be written as hₓ₊₀(ₐₓ), where mₓ₊₀(ₐₓ) is the moment of the jth atom I = X, Y, or Z in the ith shell. For the X₂Y₁₋ₓZₓ compound this relates to
follows a similar trend as the value of the mean spacing within the corresponding compound.

Using Eq. (4) and assuming unalterability of the magnetic moments one can calculate the absolute difference between adjacent lines:

\[ \Delta H(Mn^0) = -h_3m(Mn) + h_3m(Fe) = -h_3[m(Mn) - m(Fe)]. \]

(5)

According to calculations (see Ref. 1 for details), using a supercell and assuming a preferential order of Mn and Fe, only one magnetic moment for Mn and one for Fe, respectively, exists within a particular compound. This leads to mean values of the Co, Mn, and Fe magnetic moments within a particular compound. However, the small difference between the magnetic moments of Mn and Fe explains why \( H_0(Mn) \) stays nearly constant despite the alteration of the local environment, and why, thus, also the spacing between adjacent lines stays constant. Moreover, regarding the meaning of the terms in Eq. (4), one expects that the transferred hyperfine field at the \( ^{55}\text{Mn} \) nuclei for a particular compound is also constant for environments with different numbers of Mn and Fe in the third shell. Using Eq. (5) and the calculated magnetic moments, the absolute values of \( h_3 \) coefficients can be calculated (see Table I), assuming that the local hyperfine field due to the on-site Mn moment and the magnetic moments of Co, Mn, and Fe are not changed during the altering of the environment for a given compound. In summary, according to our model, the constant difference in hyperfine field between the resonance lines within a compound is mainly related to the difference of the magnetic moments of Mn and Fe.

**F. Transferred hyperfine field and band structure as a function of the overall Fe concentration**

Even though the spacing between adjacent resonance lines is approximately constant within each compound, it changes with increasing Fe concentration in the substitutional series \( \text{Co}_x\text{Mn}_{1-x}\text{Fe}_x\text{Si} \), as seen, e.g., from Table I. Figure 5(a) shows the calculated linear dependence of the Mn and Fe magnetic moments on the Fe concentration \( x \). These values were calculated by the scalar relativistic full-potential linearized augmented plane wave—+U (FLAPW + U) method, as described in Ref. 1. Using these values, one can perform a linear regression in order to estimate all magnetic moments of Mn and Fe for all Fe concentrations \( x \). This linear regression reveals that the difference between the magnetic moments of Mn and Fe is rather small with increasing concentration \( x \) while the satellite frequency spacing for a given Fe concentration is significantly decreasing [the gradient is \( -2.04 \text{ MHz}/(\text{Fe concentration } x) \)] comparing all \( \text{Co}_x\text{Mn}_{1-x}\text{Fe}_x\text{Si} \) compounds with increasing Fe concentration \( x \), and that the mean spacing significantly decreases from \( x = 0.1 \ (3.05 \pm 0.078 \text{ MHz}) \) to \( x = 0.9 \ (1.60 \pm 0.09 \text{ MHz}) \). Apparently it is valid that \( \Delta H(Mn^0)_{\text{Mn-rich}} > \Delta H(Mn^0)_{\text{Fe-rich}} \). Moreover, according to Figs. 4 and 5(b), this decrease is found to be linear as a function of the measured Fe concentration \( x \).

In particular Heusler compounds with Mn on the \( Y \) position tend to have a high, localized magnetic moment but they are also itinerant ferromagnets. This allows us to use a description based on a more local model to understand the spectra for a given Fe content \( x \), however, we need to take their itinerant character into account to explain the change of spacing with increasing \( x \). As was shown by Balke et al., with increase of the Fe concentration in \( \text{Co}_x\text{Mn}_{1-x}\text{Fe}_x\text{Si} \), there are significant changes in the density of states. With increasing Fe content, different and/or additional bands may cross the \( s \) bands and hybridize with them. Hence, the observed alteration in the spacing reflects the changes in the density of states by adding additional electrons in different bands upon the substitution of Mn by Fe. Moreover, the fact that the resonance frequencies and the corresponding local fields show a different dependence upon substitution than the \( \text{Co}_x\text{FeAl}_{1-x}\text{Si} \) series may indicate a deviation from a rigid band shift upon substitution in \( \text{Co}_x\text{Mn}_{1-x}\text{Fe}_x\text{Si} \). We will come back to the alteration of the electronic structure in Sec. II G.

**G. NMR frequency shift**

Additionally to the varying spacing, Fig. 4 also demonstrates that the resonance frequencies for a particular third shell environment slightly shift with increasing overall Fe content. Note that the frequency for a compound with Fe content \( x = 0 \) extrapolates to the value of 354.6 MHz, which is very close to the measured frequency in \( \text{Co}_x\text{MnSi} \). Each particular environment in the third shell of \( ^{55}\text{Mn} \) in a particular \( \text{Co}_x\text{Mn}_{1-x}\text{Fe}_x\text{Si} \) composition is represented by a symbol in
FIG. 6. (Color online) Shown are the $H_{hf}$ of the measured resonance lines (black squares), the mean $H_{hf}$ values of each compound, the width of their distribution (upright red lines) as well as calculated $H_{hf}$ values using the FLAPW + $U$ method (grey dots) as a function of the Fe concentration $x$. Additionally, the grey line with the grey squares represents the calculated $H_{hf}$ values using the FLAPW + $U$ method plus a constant term. This line shows that the general trend of the calculated hyperfine fields agrees well with the experimental ones and is different only by a constant shift.

**Fig. 4.** This shift is, additionally to Fig. 4, exemplarily also illustrated by the arrows in Fig. 1 for the 7 Fe + 5 Mn environment. Note that such a frequency shift is observed for all environments of the $^{55}$Mn nuclei. As can be seen, in the case of the Mn-rich environments, the resonance frequencies strongly increase with increasing overall Fe concentration $x$, while the resonance frequencies of the very Fe-rich environments (about 11 or 12 Fe atoms in the third shell) decrease slightly with increasing $x$. This dependence is also monitored by the linear fits (black lines) in Fig. 4, revealing the gradients of the linear regressions. These gradients stay almost constant at about 10 MHz/(Fe concentration $x$) for the environments with less than 2 Mn neighbors and get smaller and even negative for the environments with 10, 11, and 12 Fe atoms. This observation is related to the “bending” of the hyperfine field dependence as a function of Fe content $x$ (see Fig. 5). However, similar to the effect observed by Kawakami et al. in Co$_2$Mn$_{1−x}$Fe$_x$Ge, the general trend of the calculation, in particular if applying a constant term (dotted line with grey squares), is in line with experimental observation. The calculations underestimate the $H_{hf}$ values by a constant shift of about 53 MHz (~15%). This is a reasonable value, since we have a non-monotonic behavior. The mean $H_{hf}$ values of the $^{55}$Mn nuclei increase with increasing Fe content $x$, in agreement with the calculations. Remarkably, the general trend of the calculation, in particular if applying a constant term (dotted line with grey squares), is in line with experimental observation. The calculations underestimate the $H_{hf}$ values by a constant shift of about 53 MHz (~15%). This is a reasonable value, since there is always a deviation (up to 50%) for the hyperfine field obtained by a band-structure calculation.

**H. NMR linewidth**

The linewidth of the quaternary compounds exhibits an apparent parabolic behavior (see Fig. 7). This behavior is related to higher shell effects which contribute to the behavior of the linewidth $Γ$ (see also Refs. 16 and 17) as a function of the Fe concentration $x$. The impact of higher shells on the linewidth can be demonstrated by comparing the linewidth in the ternary compound Co$_2$MnSi with one of the quaternary compounds, such as, e.g., Co$_2$Mn$_{0.5}$Fe$_{0.5}$Si. The first resonance line in Co$_2$Mn$_{0.5}$Fe$_{0.5}$Si is attributed to Mn nuclei with no Fe atoms in the third shell, and therefore, this line also corresponds exactly to the third shell environment in unsubstituted Co$_2$MnSi. This is confirmed by the experimental observation that both lines exhibit the same resonance frequency (354.5 MHz). The linewidth in Co$_2$MnSi is very small (about 0.6 MHz), reflecting the fact that the $^{55}$Mn nuclei have only one particular
environment in the higher shells. The corresponding linewidth in Co$_2$Mn$_{0.9}$Fe$_{0.1}$Si is 1.8 MHz, reflecting the distribution of hyperfine fields due to a random distribution of the Mn and Fe atoms in higher shells (but without Fe atoms in the third shell). Note, that a small contribution to the linewidth can also be given by small lattice distortions and a concomitant change of the quadrupole splitting. This linewidth behavior is also apparent from Fig. 3, revealing that the curves of the relative distribution of Mn and Fe in the third shell are both small for the Mn- and Fe-rich ones, but comparatively broad for compounds with medium Fe concentrations.

However, the linewidth seems to be modified by at least one additional factor, namely the subline spacing. The subline spacing is larger for the Mn-rich compounds and smaller for the Fe-rich ones (see above). This might also lead to a smaller tendency to separate in Co$_2$FeSi, leading to a nonhomogenous distribution of Mn in the very Fe-rich compounds (see also discussion above).

III. SUMMARY

The local environment of the complete Co$_2$Mn$_{1-x}$Fe$_x$Si substitutional series was investigated by means of $^{55}$Mn NMR spectroscopy. Using the NMR technique, it was confirmed that the origin of the line splitting is a random distribution of Mn and Fe in third and higher shells of the $^{55}$Mn nuclei. The systematic analysis of the complete substitutional series Co$_2$Mn$_{1-x}$Fe$_x$Si showed that the spacing between adjacent resonance lines is approximately constant within a compound, and decreases with increasing overall Fe concentration $x$. This observation supports the model that neighboring Fe in the third nearest-neighbor shell contribute to a transferred hyperfine field. The decrease of the subline spacing was related to the gradual filling of different bands with different $s$ character and different hybridization with increasing Fe content $x$. The change in the density of states is also contributing to the decrease in the resonance frequencies for the Fe-rich environments, and to the shift of the whole spectrum, revealing a “bending” of the hyperfine field dependence on $x$, present in this compound. The observed bending may also reflect the transition from a more localized (Mn-rich compositions) to a more itinerant (Fe-rich compositions) character.

All results, as presented in the previous sections, unambiguously confirm the $L_2^1$ structure with a random distribution of Mn and Fe on the 4b Wyckoff position for the complete substitutional series. Band-structure calculations discussed in Ref. 1 by Balke et al. predict a very stable half metallicity of the compounds with $x \approx 0.5$. These calculations were performed using a supercell with a preferential distribution of Fe and Mn. Thus, it might be quite relevant to recalculate the band structure of Co$_2$Mn$_{1-x}$Fe$_x$Si including the experimentally verified random distribution of Mn and Fe, and to check whether the minority band gap and the half metallicity is conserved. The high structural order of all members of the substitutional series, demonstrated by the $^{55}$Mn NMR results, is one important ingredient for the possibility to observe the half-metallic character and the high degree in spin polarization of Co$_2$Mn$_{1-x}$Fe$_x$Si and illustrates that in particular the Co$_2$Mn$_{1-x}$Fe$_x$Si compounds with $x \approx 0.5$ may be ideal candidates for spintronic applications.

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