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Effects of random distribution of Mn,Fe in $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ Heusler compounds probed by ^{55}Mn nuclear magnetic resonance

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Recent spin echo nuclear magnetic resonance (NMR) revealed that the half-metallic $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ Heusler alloys exhibit the $L2_1$ structure with random distribution of Mn and Fe on the $4b$ Wyckoff position. This random distribution is most prominent in the third coordination shell of the ^{55}Mn nuclei, as this shell is the first magnetically active shell, leading to a line splitting in the ^{55}Mn NMR spectra. A comparison, as presented in this paper, of all ^{55}Mn NMR satellite lines shows that the resonance frequencies corresponding to the same number of Fe atoms in the third shell of ^{55}Mn shift to slightly different resonance frequencies with increasing overall Fe content x . This shift is related to the constructive contribution of higher shells to the hyperfine field. These higher shells affect also the satellite linewidth, leading to a parabolic behavior with increasing Fe concentration x . This parabolic behavior is modified by the frequency spacing related to the replacement of Mn by Fe.

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I. INTRODUCTION

According to band structure calculations, members of the substitutional series $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ with $x \sim 0.5$ are particular stable half-metals.¹⁻³ They belong to the class of X_2YZ Heusler compounds, crystallizing in the $L2_1$ structure. The $L2_1$ structure of the complete substitutional series $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ has recently been observed by x-ray diffraction and extended x-ray absorption fine structure.¹⁻³ From a crystallographic point of view, the $L2_1$ structure type makes it necessary that Fe and Mn occupy the $4b$ Wyckhoff position randomly.

Spin echo nuclear magnetic resonance (NMR) measurements are able to probe the direct local environments of the active atoms and are, thus, able to resolve next neighboring shells.⁴⁻⁷ Thus, this method provides a unique tool to reveal the random distribution of Mn and Fe in $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$.

Recent NMR measurements unambiguously demonstrated the expected random distribution of Mn and Fe on the $4b$ position in $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ in the third shell of ^{55}Mn .⁷ The hyperfine field is mainly determined by the influence of nearest neighbor atoms, and, therefore, the effect of a random distribution is usually observed as a first coordination shell effect.^{8,9} However, in case of the $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ compounds, the third shell is the first magnetically active shell. Therefore, the random distribution has the main impact on the third shell of ^{55}Mn .

In this paper the NMR technique was used to investigate the next neighboring and higher shells of $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$. It will be shown that the distribution of Mn and Fe affects not

only the third shell but also higher shells. In particular, this distribution is random in all shells and is described by a binomial distribution.

Polycrystalline bulk Heusler compounds were prepared as described elsewhere.^{2,10} The NMR experiments were performed in an automated, coherent, phase-sensitive spin echo spectrometer at 4.2 K. The NMR spectra were recorded in the frequency range of 350–395 MHz in steps of 0.25 MHz by means of a measurement of the spin echo intensity without external magnetic field. All NMR spectra were corrected regarding the enhancement factor as well as the f^2 dependence, resulting in relative intensities proportional to the number of nuclei with a given NMR resonance frequency.

II. RESULTS AND DISCUSSION

Figure 1 exemplarily shows the ^{55}Mn -NMR spectra of $\text{Co}_2\text{Mn}_{0.1}\text{Fe}_{0.9}\text{Si}$ (a), $\text{Co}_2\text{Mn}_{0.3}\text{Fe}_{0.7}\text{Si}$ (b), $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$ (c), $\text{Co}_2\text{Mn}_{0.7}\text{Fe}_{0.3}\text{Si}$ (d), and $\text{Co}_2\text{Mn}_{0.9}\text{Fe}_{0.1}\text{Si}$ (e). All spectra exhibit a splitting into several lines. The satellite lines in the spectra have been assigned to Mn atoms experiencing a different distribution of Mn and Fe atoms in the third coordination shell.⁷ The most prominent line of the spectra shifts to higher resonance frequencies with increasing Fe content x . Thus, the substitution of Mn by Fe increases the resonance frequency. This observation corresponds to an increase of the modulus of the hyperfine field and lines with which higher resonance frequencies, corresponding to higher hyperfine fields, are assigned to the Fe rich environments of the ^{55}Mn nuclei. The spacing between adjacent lines is almost constant within each compound. This constant spacing between subsequent lines is in agreement with the prediction within the

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FIG. 1. The ^{55}Mn spectra of $\text{Co}_2\text{Mn}_{0.1}\text{Fe}_{0.9}\text{Si}$ (a), $\text{Co}_2\text{Mn}_{0.3}\text{Fe}_{0.7}\text{Si}$ (b), $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$ (c), $\text{Co}_2\text{Mn}_{0.7}\text{Fe}_{0.3}\text{Si}$ (d), and $\text{Co}_2\text{Mn}_{0.9}\text{Fe}_{0.1}\text{Si}$ (e). The resulting Gaussians, the fits, and corresponding distribution of Mn and Fe in the third shell of ^{55}Mn are also given in (a)–(e). The dashed line illustrates the shift of the resonance frequency for the 7Fe+5Mn environment as a function of the nominal Fe concentration x .

simple model as described in Ref. 7. For further analysis, the observed lines of all spectra of the complete substitutional series were fitted using a sum of Gaussians (represented in Fig. 1 by black lines). The width of these Gaussian lines were restrained within each compound to be identical. Figure 1 also shows the corresponding distribution of Mn and Fe in the third shell of ^{55}Mn .

A comparison of the linewidth of the complete substitutional series [see Fig. 2(a)] reveals that the linewidths Γ first increase with increasing Fe concentration x and decrease after the maximum of about 2 MHz (maximum at mid-Fe range compounds). However, the linewidth of very Fe rich compounds is even smaller than the linewidth of the very Mn rich compounds.

The satellite lines corresponding to the same number of Fe atoms in the third shell of ^{55}Mn shift with increasing overall Fe content to slightly different resonance frequencies. This is illustrated by the dashed line in Fig. 1 for the 7Fe+5Mn environment, but this frequency shift is observed for all environments of the ^{55}Mn nuclei. Note that the very Fe rich environments are not observed for the low Fe concentration compounds and that the very Mn rich environments are not observed for the high Fe concentration compounds, respectively. In order to make this slight frequency shift more obvious, Fig. 2(b) exemplarily shows the resonance frequencies for three environments in the third shell of ^{55}Mn as a function of the optimized Fe concentration x . Optimization of the nominal Fe concentration x was done by means of an optimization of the matching of the intensity predicted by

FIG. 2. Width of the Gaussian lines obtained from fits of the substitutional series $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ as a function of the Fe concentration x (a). The line is drawn to guide the eye. The resonance frequencies of the $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ alloys (measured at the ^{55}Mn atoms) exemplarily for three particular environments of the third shell of ^{55}Mn as a function of the optimized Fe concentration x and their linear fits (b). Each symbol corresponds to a $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ alloy with an optimized Fe concentration x . The lines are drawn to guide the eye.

binomial distribution with regards to the experimental data by varying the Fe concentration x . This optimization was monitored by the least square method (see Ref. 7 for details).

Each symbol in Fig. 2(b) corresponds to a particular environment in the third shell of ^{55}Mn in a particular $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ compound. In line with Fig. 1, Fig. 2(b) demonstrates that the satellite lines slightly shift to different resonance frequencies with increasing overall Fe content. This linear dependence is in principle obtained for all resonance frequencies as a function of the Fe concentration for all environments in the third shell of ^{55}Mn .

The shift of the satellite lines for the same number of Fe next neighbors may be caused by two different effects. First, the lattice parameter decreases from Co_2MnSi to Co_2FeSi from 5.65 Å (Ref. 11) to 5.64 Å (Ref. 1) and this may contribute to the slight frequency shift. But more importantly, the substitution of Y by Y' may not only affect the composition of the third coordination shell of ^{55}Mn but may also affect the composition of higher shells, which may explain the shift of the resonance frequencies, as will be further explained below.

As mentioned before the third shell of Mn is the first magnetically active shell. Thus, the random distribution has the main impact on the third shell of Mn. However, the ran-

dom distribution of Mn and Fe located in more distant shells will contribute in a cumulative way leading to a shift of the resonance frequency corresponding to equal third shell environments but with different higher shell distributions of Mn and Fe. Thus, each satellite arising from the random distribution of Mn and Fe in the third shell of Mn consists of unresolved subsatellites arising from the random distribution of Mn and Fe in higher shells. Note that the distribution of the atoms is supposed to be random in all shells and is described by a binomial distribution.

These higher shell effects also contribute to the behavior of the linewidth Γ as a function of the Fe concentration x ,¹² which will be explained in the following. In order to take higher shells into account, the binomial distribution as given in Ref. 7 has to be modified. As an example, the sixth shell, which is the next magnetically contributing shell, consisting of $6Y$, is chosen in order to demonstrate the effect of higher shells on the probabilities to find a particular surrounding of the form $[nY' + (12-n)Y]$ atoms in the third shell + $[kY + (6-k)Y']$ atoms in the sixth shell of the Y^0 atom, leading to a modified binomial distribution,

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

with $N=12$ and $K=6$ with respect to the number of sites on the corresponding shells and with x the overall concentration of the Y' atoms.

According to Eq. (1), the probability to observe all underlying lines arising from higher shell effects is the highest for the mid-Fe range compounds and lower for all compounds with more or less Fe. This reveals the largest width to be found for the mid-Fe compositions in agreement with the experimental observations. However, the width is modified by at least one additional factor, namely, the frequency spacing. As already mentioned above, the spacing between adjacent lines is almost constant within each compound in agreement with the model, as described in Ref. 7. However, the frequency spacing is larger for the Mn rich compounds and smaller for the Fe rich ones. This influence of the frequency spacing will be a subject of further analysis.¹³ Overall, the width depends on the substitution of Mn by Fe described by binomial distribution, leading to the experimentally observed parabolic broadening with an additional modulation of the frequency spacing.

These results confirm the random distribution of Mn and Fe in $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ Heusler compounds in all shells in agreement with previous results.⁷

III. SUMMARY

In summary, the effects of the random distribution of Mn and Fe in $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ Heusler compounds ($L2_1$ structure type) of the resonance frequencies has been analyzed. The shift of the satellite lines corresponding to the same number of Fe atoms in the third shell of ^{55}Mn with increasing overall Fe content could be attributed to the random distribution of Mn and Fe in higher shells. This higher shell effects also explain the experimentally observed behavior of the linewidth with increasing Fe concentration x with an additional modulation of the frequency spacing. This modulation causes the linewidth of very Fe rich compounds to be even smaller than the linewidth of the very Mn rich compounds.

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