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Probing the random distribution of half-metallic $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ Heusler alloys

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$\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ Heusler alloys crystallize in the $L2_1$ structure. This structure type requires random distribution of Mn and Fe in case of the mixed alloys. The spin echo nuclear magnetic resonance (NMR) technique probes the direct local environments of the active atoms and is thus able to resolve next neighboring shells providing a unique tool to verify the random distribution of Mn and Fe in $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$. Exemplarily, the half-metallic quaternary Heusler alloy $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$ was investigated by means of NMR. The ^{55}Mn NMR measurements unambiguously demonstrate the random distribution of Mn and Fe on the $4b$ Wyckoff position in $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$. © 2007 American Institute of Physics. [DOI: 10.1063/1.2760158]

For most technical applications half-metallic ferromagnets with a high thermal stability of the minority-spin band gap and thus a robust half-metallic behavior are favored.^{1,2} Therefore, compounds with the Fermi energy located at the middle of the band gap are highly preferred.^{1,2} If the Fermi energy is near one of the edges, the band gap may easily be smeared out at finite temperatures or destroyed by quasiparticle excitation.^{1,2} According to band structure calculations, members of the substitutional series $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ with $x \sim 0.5$ belong to this particular stable half-metals. However, the $L2_1$ structure of the complete substitutional series is observed by x-ray diffraction and extended x-ray-absorption fine structure.^{1,3,4} 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.⁵⁻⁷ Thus this method provides a tool to reveal the random distribution of Mn and Fe in $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$. NMR measurements provide a tool to obtain the local environment by measuring the resonance frequencies and consequently probing the local hyperfine magnetic fields, revealing the first few next neighboring shells of the active atoms.

In this letter, the NMR technique was used to investigate the local environment of $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$, mainly concentrating on $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$, as a representative of the complete substitutional series. In particular, the focus will be on measurements of the ^{55}Mn nuclei, though the NMR measurements of the ^{59}Co nuclei lead to similar results. It will be shown that the NMR technique is indeed a very suitable tool to uniquely confirm the expected random distribution in $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$.

Polycrystalline bulk Heusler compounds were prepared as described elsewhere.^{1,8} The NMR experiments were performed in an automated, coherent, spin echo spectrometer at 4.2 K. The NMR spectra were recorded in the frequency range of 350–390 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 frequency.

In case of a $L2_1$ ordered X_2YZ compound the first coordination sphere of the Y (Wyckhoff position $4b$) atoms consists of 8 X atoms ($8c$) in a distance of $a\sqrt{3}/4$, the second one is built up by 6 Z atoms ($4a$) at $a/2$, and the third consists of 12 Y atoms at $a\sqrt{1}/2$, where a is the cubic lattice parameter. A partial substitution of Y atoms by Y' atoms in $X_2Y_{1-x}Y'_xZ$ will thus change the third coordination shell of the Y^0 atom assumed to be at the origin. If the Y' atoms replace part of the Y atoms randomly, one expects that the Y^0 atom can be surrounded by 0 Y' +12 Y , 1 Y' +11 Y , 2 Y' +10 Y , ..., or 12 Y' +0 Y third nearest neighbors, leading to 13 different possibilities for different surroundings of a Y atom if restricting to the third shell.

The probability $P(n, x)$ for a particular surrounding of the form nY' atoms+(12- n) Y atoms in a certain shell of the Y^0 atom is given by a binomial distribution which depends on the concentration x of the Y' atoms.^{5,9} If applied to this particular probability to find n Mn and (12- n)Fe on the 12 positions of the third neighbor shell of the ^{55}Mn nuclei if assuming $L2_1$ structure is given by

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

These probabilities can be directly compared to the intensities of a spin echo NMR measurement,¹⁰ while the corresponding resonance frequencies are related to the hyperfine

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FIG. 1. Spin echo intensity as a function of frequency for ^{55}Mn in $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$ (black dots) and the fit (gray line) resulting from Gaussians (black lines). The distribution of Mn and Fe atoms in the third coordination shell of the ^{55}Mn is given for each line as well as the relative areas obtained from Gaussians.

fields of the active atom in this certain environment as explained in the following.

The hyperfine field experienced by the Y^0 atom will depend on a particular environment and one expects that the effective hyperfine field at the atom Y^0 is composed of the on-site hyperfine field H_0 and the transferred contact hyperfine fields emerging from the magnetic moments of the surrounding atoms as follows:¹⁰

$$H(Y^0) = H_0 + H_1 + H_2 + H_3 + \dots = \sum H_i, \quad (2)$$

where the indices are for the i th shell. In a simple model, each contact hyperfine field term may be written as $h_i \sum m_{i,j}(I)$, where $m_i(I)$ is the moment of the atom $J=X, Y$, or Z in the i th shell. For the $X_2Y_{1-x}Y'_xZ$ compound in the lowest approximation this relates to (if neglecting the terms arising from the Z element, which does not contribute to the magnetic moment)

$$H(Y^0) = H_0(Y) + 8h_1m(X) + h_3((12-n)m(Y) + nm(Y')). \quad (3)$$

According to this, one expects a constant splitting of the lines if one assumes that the magnetic moments and $H_0(Y)$ do not change with the change in the environment.^{10,11} Although Eq. (3) will be used throughout the further analysis, it should be mentioned that it is a very simple model and a complete description should also include the change of the local magnetic moments and hyperfine fields with the alteration of the environment.

Figure 1 shows the ^{55}Mn -NMR spectrum of $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$, as representative for the complete substitutional series. The spectrum exhibits several lines which has been assigned to Mn atoms experiencing a different distribution of Mn and Fe atoms in the third coordination shell. A constant spacing of about 2.35 ± 0.09 MHz between subsequent lines is in agreement with the constant spacing predicted within the simple model introduced in Eq. (3). From Eq. (3), it is further expected that the absolute difference between adjacent lines is $\Delta H(\text{Mn}^0) = -h_3m(\text{Mn}) + h_3m(\text{Fe}) = -h_3(m(\text{Mn}) - m(\text{Fe}))$. Using the calculated values for the magnetic moments of Mn ($3.07\mu_B$) and Fe ($3.37\mu_B$),¹ one

FIG. 2. Relative areas of the resonance lines as a function of the number of Fe atoms in the third coordination shell of ^{55}Mn . The black full symbols represent the fitting results, while the gray blank symbols correspond to binomial distributions. Shown are the results for the $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$ compound with ideal stoichiometry $x=0.5$ (squares) and optimized stoichiometry $x=0.517$ (triangles), $\text{Co}_2\text{Mn}_{0.7}\text{Fe}_{0.3}\text{Si}$ and $\text{Co}_2\text{Mn}_{0.3}\text{Fe}_{0.7}\text{Si}$ both in comparison with their corresponding optimized stoichiometry [$x=0.318$ (stars), and $x=0.68$ (circles)]. The lines are drawn to guide the eye.

finds that $|h_3| = 0.58 \times 10^6 \text{ A/m } \mu_B$ for $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$. Please note that from the single experiment with $x=0.5$ the sign of the hyperfine field cannot be determined. However, with regard to the results of the complete substitutional series, the substitution of Mn by Fe increases the resonance frequency. This observation corresponds to an increase of the modulus of the hyperfine field. Taken the negative and dominant character of $H(\text{Mn}^0)$,¹⁰ as well as the measurements for all $\text{Co}_2\text{Mn}_{1-x}\text{Fe}_x\text{Si}$ Heusler alloys into account, it turns out that h_3 is negative in agreement with the results of Khoi *et al.*¹⁰ Lines with higher resonance frequencies, corresponding to higher hyperfine fields, are assigned to the Fe rich environments of the ^{55}Mn nuclei, in agreement with the results of the complete substitutional series. The small difference between the magnetic moments of Mn and Fe explains why $H_0(\text{Mn})$ stays nearly constant and why the spacing between adjacent lines stays constant, too.

For further analysis, the observed lines were related to a binomial distribution as given in Eq. (1). Therefore the spectrum was fitted using a sum of Gaussians (gray line in Fig. 1) with fixed width. The resulting Gaussians and their relative contributions are also given in Fig. 1. In addition, the different local environments of the third coordination shell of the ^{55}Mn nuclei are illustrated schematically in Fig. 1. The main satellite with a relative area of $23.24 \pm 0.09\%$ has the resonance frequency of 375.2 MHz arising from ^{55}Mn nuclei with 6 Fe+6 Mn next neighbors, representing the preferentially ordered $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$ alloy. This particular local environment of the ^{55}Mn nuclei corresponds to a hyperfine field of 28.3 MA/m. This value is larger than calculated for $\text{Co}_4\text{MnFeSi}_2$ (24.27 MA/m) with the same stoichiometry but in a preferentially ordered structure.

Figure 2 shows the relative areas obtained by Gaussians fits of $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$, $\text{Co}_2\text{Mn}_{0.7}\text{Fe}_{0.3}\text{Si}$, and $\text{Co}_2\text{Mn}_{0.3}\text{Fe}_{0.7}\text{Si}$ of the ^{55}Mn measurement (black dots) as well as the corresponding binomial distributions (gray open symbols). The shape of all experimental distribution curves (black full symbols) follows the calculated binomial distribution (gray blank symbols). This confirms the predomi-

nantly random distribution of Mn and Fe on the $4b$ position in agreement with the results of the complete substitutional series. The maxima of these curves shift to higher numbers of Fe atoms with increasing overall Fe content. This follows from the fact that an overall high Fe content leads locally to a larger number of Fe neighbors. In addition, a comparison of the experimental results with the binomial distribution curves explains the observation of less than 13 lines in all ^{55}Mn spectra, as the probabilities for some particular surroundings are too low to be observed in the NMR experiment. In the following, the focus will be the analysis of results of $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$. The NMR experiment of $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$ exhibits a slight asymmetry of the relative areas, with larger contributions of the satellites corresponding to higher numbers of Fe neighbors. This minor imbalance of the relative areas is caused by a deviation of the ideal stoichiometry. Optimization of the fraction x by means of a least squares method revealed the fraction x of this particular sample to be $x=0.517\pm0.004$ (gray open triangles in Fig. 2). This small deviation from the nominal stoichiometry ($x=0.5$) might be due to the accuracy of the stoichiometry in the preparation process, and might change from sample to sample. Moreover, due to the fact that the nominal values are very close to the one obtained by binomial distributions these particular samples may be used to represent the ideal stoichiometries in further experiments.

These results unambiguously confirm the $L2_1$ structure with random distribution of Mn and Fe on the $4b$ Wyckhoff position of $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$. However, the band structure calculations,¹ predicting a very stable half-metallicity of $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$, were performed on the base of a preferential distribution of Fe and Mn. Thus, it might be very relevant to recalculate the band structure of $\text{Co}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{Si}$ including the experimentally verified random distribution of Mn and Fe, and to check whether the minority band gap and the half-metallicity is conserved. However, taking the band structure calculations of the complete substitutional series into account, it seems to be likely that implementation of the random distribution will have no consequences for the very stable half-metallicity of $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$. Thus, the high

crystallographic order of $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$ demonstrated by the ^{55}Mn NMR results will have a strong impact on the half-metallic character and the high degree of spin polarization of $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$, including the expectation of high tunneling magnetoresistance ratios, and illustrates that $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$ could be an ideal candidate for spintronic applications.

In summary, it has been demonstrated that ^{55}Mn NMR is a suitable tool to probe the local environment of the NMR active atoms in Co_2 based Heusler compounds. In addition, it was shown that NMR is a useful method to accurately extract the fraction of x in various substitutional series. In particular, using the NMR technique it was observed that $\text{Co}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{Si}$ ($L2_1$ structure type) shows the expected random distribution of Mn and Fe on the $4b$ position which reveals that this quaternary alloy is very well ordered and thus potentially enables stable half-metallicity including a very high spin polarization.

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