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

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Co$_2$Mn$_{1-x}$Fe$_x$Si Heusler alloys crystallize in the $L_2_1$ 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 Co$_2$Mn$_{1-x}$Fe$_x$Si. Exemplarily, the half-metallic quaternary Heusler alloy Co$_2$Mn$_{0.5}$Fe$_{0.5}$Si was investigated by means of NMR. The $^{55}$Mn measurements unambiguously demonstrate the random distribution of Mn and Fe on the $4b$ Wyckoff position in Co$_2$Mn$_{0.5}$Fe$_{0.5}$Si.

Polycrystalline bulk Heusler compounds were prepared as described elsewhere. 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 $L_2_1$ ordered $X_2YZ$ compound the first coordination sphere of the $Y$ (Wyckoff position $4b$) atoms consists of 8 $X$ atoms ($8c$) in a distance of $a\sqrt{3}/4$, the second one is built up by $6Z$ atoms ($4a$) at $a/2$, and the third consists of $12Y$ atoms at $a/\sqrt{12}$, where $a$ is the cubic lattice parameter. A partial substitution of $Y$ atoms by $Y'$ atoms in $X_2Y_{1-x}Y'Z$ will thus change the third coordination shell of the $Y'$ atom assumed to be at the origin. If the $Y'$ atoms replace part of the $Y$ atoms randomly, one expects that the $Y'$ atom can be surrounded by $0Y'+12Y$, $1Y'+11Y$, $2Y'+10Y$, ..., or $12Y'+0Y$ 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 $Y'$ atom is given by a binomial distribution which depends on the concentration $x$ of the $Y'$ atoms. 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 $L_2_1$ structure is given by

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

These probabilities can be directly compared to the intensities of a spin echo NMR measurement, while the corresponding resonance frequencies are related to the hyperfine frequency $f$. The enhancement factor $f$ is $f(N) = \left(\frac{N}{10}\right)^3$.
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

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

where the indices are for the $i$th shell. In a simple model, each contact hyperfine field term may be written as $h_i \sum m_i(I)$, where $m(I)$ is the moment of the atom $J=X, Y, \text{or } Z$ in the $i$th shell. For the $X_2Y_1Z_0$ 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)

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

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 $^{55}\text{Mn-NMR}$ spectrum of Co$_2$Mn$_{0.5}$Fe$_{0.5}$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 adjacent 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 $\Delta H(Mn^0) = -h_3m(Mn) + h_3m(Fe) = -h_3(m(Mn) - m(Fe))$. Using the calculated values for the magnetic moments of Mn (3.07μ$_B$) and Fe (3.37μ$_B$), one finds that $|h_3|=0.58 \times 10^6 \text{ A/m } \mu_0$ for Co$_2$Mn$_{0.5}$Fe$_{0.5}$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 $H(Mn^0)$, as well as the measurements for all Co$_{2-x}$Fe$_x$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 $^{55}\text{Mn}$ nuclei, in agreement with the results of the complete substitutional series. The small difference between the magnetic moments of Mn and Fe explains why $H_0(Mn)$ 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 $^{55}\text{Mn}$ nuclei are illustrated schematically in Fig. 1. The main satellite with a relative area of 23.24±0.09% has the resonance frequency of 375.2 MHz arising from $^{55}\text{Mn}$ nuclei with 6 Fe+6 Mn next neighbors, representing the preferentially ordered Co$_2$Mn$_{0.5}$Fe$_{0.5}$Si alloy. This particular local environment of the $^{55}\text{Mn}$ nuclei corresponds to a hyperfine field of 28.3 MA/m. This value is larger than calculated for Co$_2$Mn$_{0.3}$Fe$_{0.7}$Si of the $^{55}\text{Mn}$ measurement (gray open symbols) but in a preferentially ordered structure.

Figure 2 shows the relative areas obtained by Gaussians fits of Co$_2$Mn$_{0.5}$Fe$_{0.5}$Si, Co$_2$Mn$_{0.5}$Fe$_{0.5}$Si, and Co$_2$Mn$_{0.5}$Fe$_{0.7}$Si of the $^{55}\text{Mn}$ 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 predominate
ently 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 Co$_2$Mn$_{0.5}$Fe$_{0.5}$Si. The NMR experiment of Co$_2$Mn$_{0.5}$Fe$_{0.5}$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 L$_2$$_1$ structure with random distribution of Mn and Fe on the 4b Wyckhoff position of Co$_2$Mn$_{0.5}$Fe$_{0.5}$Si. However, the band structure calculations$^1$, predicting a very stable half-metallicity of Co$_2$Mn$_{0.5}$Fe$_{0.5}$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 Co$_2$Fe$_{0.5}$Mn$_{0.5}$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 Co$_2$Mn$_{0.5}$Fe$_{0.5}$Si. Thus, the high crystallographic order of Co$_2$Mn$_{0.5}$Fe$_{0.5}$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 Co$_2$Mn$_{0.5}$Fe$_{0.5}$Si, including the expectation of high tunneling magnetoresistance ratios, and illustrates that Co$_2$Mn$_{0.5}$Fe$_{0.5}$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 Co$_2$Mn$_{0.5}$Fe$_{0.5}$Si (L$_2$$_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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