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# Average Magnetization and Fe Hyperfine Fields in $Co_2FeSi$-based Heusler Alloys

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In the present study SQUID magnetic and $^{57}$Fe Mössbauer measurements were performed on bulk $Co_2FeAl_{1-x}Si_x$, $Co_2Fe_{0.9}TM_{0.1}Si$ (TM = Ti, V, Cr, Mn, Co, Ni, Cu), $Co_{2-y}Fe_{1+y}Si$ and $Co_2Fe_{1+z}Si_{1-z}$ samples prepared by induction melting. The $Co_2FeAl_{1-x}Si_x$ shows the $L2_1$ crystal structure only for $x \geq 0.5$, between $x = 0$ and 0.3 it has the B2 structure (Fe–Al, Si disorder). The average magnetization of these alloys does not follow the expected Slater-Pauling trend (on the Si side saturation is observed around 5.75 $\mu_B$/f.u.) and similar deviation is observed for the replacement of Fe by transition metal (TM) atom. The effect of the antisite disorder (Fe–Si) on the magnetization and Fe hyperfine parameters was determined and significant decrease in the Co magnetic moment for excess Si neighbourhood is extrapolated. The formerly reported large $\approx 6$ $\mu_B$/f.u. magnetization for $Co_2FeSi$ was observed only in samples having Fe excess and Si deficiency.

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## 1. Introduction

Half metallic ferromagnetic alloys are indispensable for spintronic applications. Large number of the ternary $X_2YZ$ Heusler alloys (where X and Y are transition metals and Z is a main group element) crystallizing in the $L2_1$ structure is predicted to have half metallic properties [1]. The $Co_2$-based Heusler alloys are especially promising materials since high Curie temperatures and magnetic moments are desirable for applications. Theoretically these Heusler alloys show a Slater-Pauling behaviour and the total magnetic moment per formula unit ($M$) scales with the total number of valence electrons ($Z_t$) following the rule: $M = Z_t - 24$ [1]. This requirement results in $M = 6$ $\mu_B$ for $Co_2FeSi$ and the reported $5.97 \pm 0.05$ $\mu_B$ value was considered as a conclusive proof of the half metallic nature of this compound [2]. Electron doping (Si–Al substitution) stabilizes the gap in the minority states and the magnetic moments follow the Slater-Pauling rule in the $Co_2FeAl_{1-x}Si_x$ system according to the electronic structure calculations [3]. Conflicting magnetic data are reported for this system. The magnetic moments measured by Balke et al. [4] follow eminently above x $\geq$ 0.4 the expected Slater-Pauli curve, while those of Refs. [5, 6] deviate from that behaviour, in these measurements the magnetic moment of $Co_2FeSi$ is significantly less than the predicted 6 $\mu_B$. Recent X-ray magnetic linear dichroism [7] and point-contact Andreev reflection spectroscopy [8] studies question the half metallic nature of $Co_2FeSi$, as well as the theoretical foundation of the calculations leading to this prediction. On the other hand, electrical transport measurements report [9] on half-metallicity with an unexpectedly small gap. This controversion motivates the present, careful magnetic and Mössbauer study of the $Co_2FeSi$ and related alloys.

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## 2. Experimental

The $Co_2FeAl_{1-x}Si_x$, $Co_2Fe_{0.9}TM_{0.1}Si$ (TM = Ti, V, Cr, Mn, Co, Ni, Cu), $Co_{2-y}Fe_{1+y}Si$ and $Co_2Fe_{1+z}Si_{1-z}$ samples were prepared via induction melting under Ar atmosphere in a cold crucible. The melting was carried out four times to ensure the homogeneity of the alloy. The weight loss during melting was less than 0.1%. In the magnetic measurements small piece of the ingots was used. X-ray diffraction, Mössbauer measurements and magnetic measurements were performed on the powder samples obtained by hand milling of this ingot in a ceramic mortar. The magnetic properties were investigated using a SQUID magnetometer (MPMS-5S) up to 5 T in the temperature range of 5–300 K, the saturation values of the formula units, $M$ will be given. The details of the measurement and calculation of the saturation moment are described elsewhere [10]. The $^{57}$Fe Mössbauer measurements were carried out by a conventional constant acceleration-type spectrometer using a closed-cycle cryostat (APD) in the temperature range 11–300 K, the given values of Fe hyperfine field, $B_{hf}$ and Fe isomer shift, IS refer to 11 K. The latter is measured with respect to $\alpha$-Fe at room temperature.

## 3. Results

Figure 1 shows the composition dependence of the magnetic moment, $M$, Fe hyperfine field, $B_{hf}$ and Fe isomer shift, IS for the $Co_2FeAl_{1-x}Si_x$ alloys. According to the X-ray diffraction, for $x \geq 0.5$ was found the $L2_1$ crystal structure: below this composition only the (200) superlattice reflection was observed (the (111) superlattice reflection characteristic of the $L2_1$ structure was missing). It means that on the Al-side the Fe, Al and Si distribution is disordered in the Co-formed cube centers corresponding to the B2 structure. This is in agreement with the former [4–6] reports. On the other hand, $M$ deviates significantly from the Slater-Pauling behaviour reported by Ref. 4; it shows saturation well

below 6 $\mu_B$, similarly to those of Refs. 5 and 6. The $B_{hf}$, which is related to the local iron magnetic moment, follows the same composition trend, thus contradicts the notion of half metallicity. It is worth emphasizing that the Fe isomer shift which measures the strength of the s-d hybridization (i.e. the re-arrangement of the s-d electrons at the Fe sites) changes linearly with the composition and shows only a break at the B2-$L2_1$ transition. The linear composition dependence of IS in the $L2_1$ structure (hybridization) against the saturating $B_{hf}$ (Fe magnetic moment) is a strong argument against the half-metallic electron structure in this system.

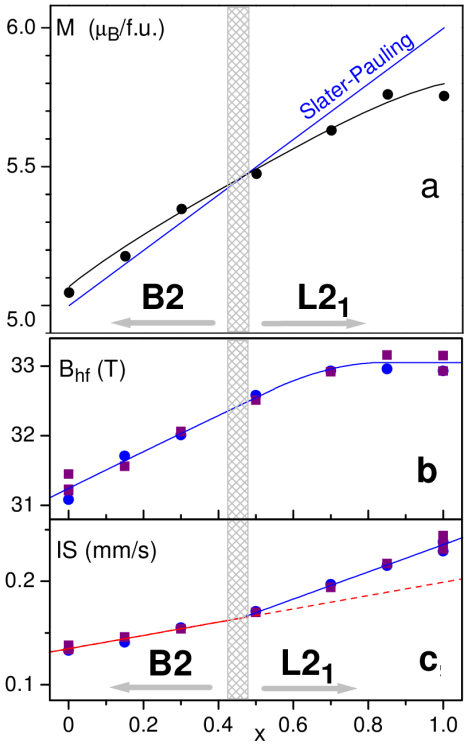


Fig. 1. Composition dependence of the average magnetic moment, $M$ (a) and the Fe hyperfine field, $B_{hf}$ (b) and Fe isomer shift, IS (c) in the $Co_2FeAl_{1-x}Si_x$ alloys. B2 and $L2_1$ show the corresponding crystal structure as explained in the text. The linear composition dependence of the Slater-Pauling behaviour of $M$ is also shown.

The former conclusion is supported when Fe is replaced by 3d elements (Fig. 2): $M$ does not show the expected Slater-Pauling behaviour. It is remarkable the observed symmetric $Z_t$ dependence. $B_{hf}$ is insensitive for the 3d substitution. This signifies a rather well localized Fe magnetic moment: although the substituted 3d atom is rather far from Fe (the first and second neighbours are Co and Si, respectively), the significant decrease in the Co magnetic moments due to this replacement is absent in $B_{hf}$. Although $M$ is symmetric as a function of $Z_t$, the change does not scale with +1 on the left, and with –1 on the right side which would correspond to the filling of the spin-up and spin-down band, respectively.

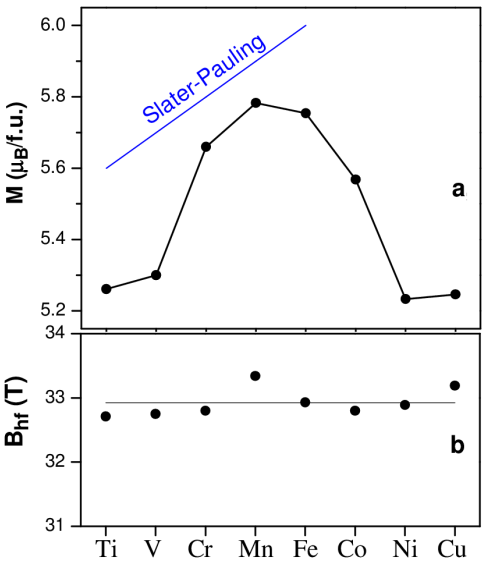


Fig. 2. Average magnetic moment, $M$ (a) and the Fe hyperfine field, $B_{hf}$ (b) of the $Co_2Fe_{0.9}TM_{0.1}Si$ (TM = 3d element) alloys. The expected Slater-Pauling dependence is also shown.

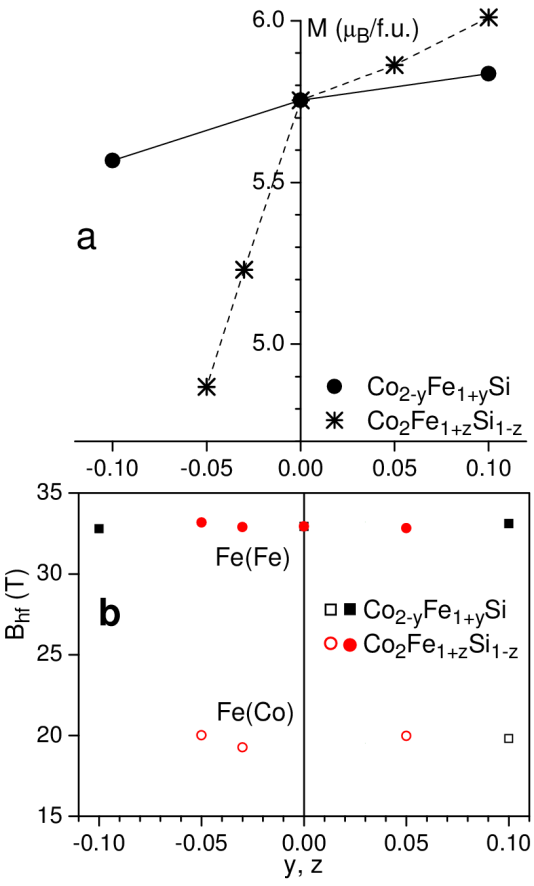


Fig. 3. Dependence of the average magnetic moment, M (a) and Fe hyperfine field, $B_{hf}$ (b) on the stoichiometry. The empty symbols in (b) correspond to the hyperfine fields of Fe atoms located on Co sites.

The value of $B_{hf}$, i.e. that of the Fe magnetic moment remains unchanged when the effect of nonstoichiometry is investigated (Fig. 3): it is valid not only for the Fe atoms located on the stoichiometric Fe sites but for the Fe atoms which replace Co atoms, Fe(Co) sites. Not unexpectedly, $M$ is increasing for excess Fe and decreasing for excess Co, but the largest decrease is caused by excess Si. Since the Fe magnetic moments are insensitive for the excess Si, it means a significant decrease in the Co magnetic moments.

## 4. Conclusions

The present magnetic and Mössbauer study contradicts the hypothesis that $Co_2FeSi$ is a half metallic alloy. It is shown that deviation from the stoichiometry, excess Fe and deficiency in Si will result in significant increase in the average magnetic moment of the alloy. Figure 4 illustrates that small deviation in composition (well within the accuracy of the chemical analysis) will result in the theoretically expected 6 $\mu_B$ value. The saturation magnetization of $Co_2FeSi$ (stoichiometric composition) and $Co_2Fe_{1.1}Si_{0.9}$ was measured to be $158.9 \pm 0.8$ emu/g ($5.75 \pm 0.03$ $\mu_B$) and $164.0 \pm 0.8$ emu/g ($6.01 \pm 0.03$ $\mu_B$), respectively.

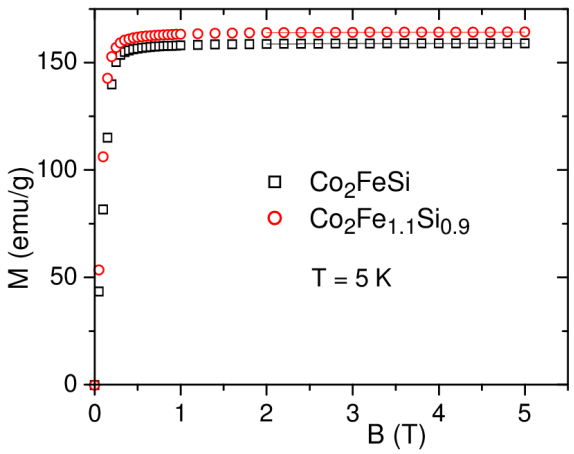


Fig. 4. Magnetization as a function of applied field for $Co_2FeSi$ and $Co_2Fe_{1.1}Si_{0.9}$. The solid lines are fits to the law of approach to saturation.

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