Half-metallic ferromagnetism with high magnetic moment and high Curie temperature in Co$_2$FeSi

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Co$_2$FeSi crystallizes in the ordered L2$_1$ structure as proved by X-ray diffraction and Mößbauer spectroscopy. The magnetic moment of Co$_2$FeSi was measured to be about 6$\mu_B$ at 5K. Magnetic circular dichroism spectra excited by soft X-rays (XMCD) were taken to determine the element specific magnetic moments of Co and Fe. The Curie temperature was measured with different methods to be (1100 ± 20)K. Co$_2$FeSi was found to be the Heusler compound as well as the half-metallic ferromagnet with the highest magnetic moment and Curie temperature.

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I. INTRODUCTION

Heusler compounds are ternary intermetallics with the composition X$_2$YZ [1]. They order in the L2$_1$ structure, space group Fm$m$m. The Co$_2$ based Heusler compounds are of particular interest due to their high Curie temperatures and the high magnetic moments per unit cell (for a review see Ref. [2, 3]).

Half-metallic ferromagnets (HFM) are predicted to be 100% spin polarized [4]. In those materials, the majority electrons are metallic whereas the minority electrons are semi-conducting or insulating. A high degree of spin polarization is interesting for various applications in magneto-electronics (for examples see [5]). Several materials in the class of Heusler compounds were predicted to be half-metallic ferromagnets [4-6].

This work reports about the Heusler compound Co$_2$FeSi that is found to be, at present, the Heusler compound exhibiting the highest magnetic moment as well as the highest Curie temperature.

II. RESULTS AND DISCUSSION

Co$_2$FeSi samples were prepared by arc-melting of stochiometric quantities of the pure metals in an argon atmosphere, followed by annealing in sealed quartz tubes at 1300K for 21 days. The crystal structure of the polycrystalline ingots was investigated by X-Ray diffraction and proved to exhibit the correct L2$_1$ structure. The lattice constant was found to be 5.64Å by Rietveld refinement. The Rietveld refinement allowed for a B2 type disorder of only < 10% (mixing between Fe and Si). $^{57}$Fe Mößbauer spectroscopy was performed to gain additional structural information. The derived spectrum (not shown here) exhibited a single sextet consisting of sharp lines with a width of 0.15mm/s being in the order of the α-Fe line width (0.136mm/s). This observation confirms the occupation of a single site for Fe and thus a well ordered system. DO$_2$ like disorder (mixing of Co and Fe at X and Y sites) can be excluded from a comparison of the measured (26.3 × 10^6A/m) and calculated values (21 × 10^6A/m for Fe in Y and 11 × 10^6A/m for Fe in X positions) of the hyperfine field.

Low temperature magnetometry was performed using a super-conducting quantum interference device (SQUID). The results are displayed in Fig.1.

![Magnetization of Co$_2$FeSi](image)

FIG. 1: Magnetization of Co$_2$FeSi. (a) shows the low temperature and (b) the high temperature magnetic properties as measured by SQUID and VSM, respectively.

The field dependence of the magnetization is typical for a soft-magnetic material. The measured magnetic moment in saturation is (5.97 ± 0.05)$\mu_B$ at 5K resulting in 6$\mu_B$ at 0K by extrapolation. This value is in agreement
with the spin moment expected from the Slater-Pauling rule. The measured magnetic moment is an integer within the experimental uncertainty, as expected for a half-metallic ferromagnet.

X-ray Magnetic Circular Dichroism (XMCD) in photo absorption (XAS) was measured at the First Dragon beamline of NSRRC (Hsinchu, Taiwan). The XAS and XMCD spectra were taken at the L_{2,3} absorption edges of Fe and Co. The results are shown in Fig. 2.

The two white lines corresponding to the L edges are clearly seen for Fe (a) and Co (b). An additional spectral feature is visible 3.5eV below the L_3 absorption edge of Co and a weaker one at the Fe L_3 edge. This feature is related to the L_2 structure and demonstrates the high structural order of the sample (it vanishes for B2 like disorder).

The magnetic moments per atom derived from a sum rule analysis for Fe and Co at \( T = 300 K \) and \( \mu_0 H = 0.4T \). The error arises mainly from the unknown number of holes in the 3d shell and the disregard of the magnetic dipole term in the sum rule analysis. The orbital to spin magnetic moment ratios are about 0.05 for Fe and 0.1 for Co. The measured ratio between the Fe and Co spin moments of 2.15 is fully reproduced by the calculated ratio of 2.18.

A seeming linear dependence of the Curie temperature as a function of the magnetic moment is observed in Co_{2}FeSi based Heusler compounds as shown in Fig. 3. One expects that \( T_C \) is highest for those HMF exhibiting a large magnetic moment. \( T_C \) should be above 1000K in Co_{2}FeSi with a magnetic moment of \( 6\mu_B \). Following this suggestion, the ferromagnetic Curie temperature of Co_{2}FeSi was measured with a vibrating sample magnetometer (VSM) equipped with a high temperature stage. The result obtained in a constant induction field of \( \mu_0 H = 0.1T \) is shown in Fig. 4. A value of \( (1100 \pm 20)K \) is obtained from the measurement.

The paramagnetic Curie-Weiss temperature \( \Theta \) was estimated from a plot of the inverse susceptibility \( 1/\chi \) as a function of temperature (see Fig. 5a). The Curie-Weiss temperature is found by interpolating \( 1/\chi(T) \) to be \( (1150 \pm 50)K \). A true linear behavior for \( 1/\chi \) as a function of temperature is not observed here because the experiment was performed in a temperature range close to the Curie temperature. A linear dependence can be expected from molecular field theory only for temperatures far above \( T_C \).

The here observed properties of Co_{2}FeSi are in agreement to those reported previously by Niculescu et al. for a higher degree of disorder (10% B2 plus 16% DO_{3}).

SQUID magnetometry does often not allow to determine high temperature magnetic phase transitions. The low temperature requirement of the instrumental set-up may not be met, in particular if \( T_C \) is very high. Differential scanning calorimetry (DSC) is well established to investigate various kinds of phase transitions in solid materials (for example see: [14]). Here it was used to examine the magnetic phase transition in order to support the Curie temperature received by the VSM experiments. Fig. 3 compares the DSC signal (b) with the derivative of the specific magnetization (a) with respect to the temperature (compare Fig. 4). The minimum at \( (1040 \pm 20)K \) in Fig. 3a corresponds to the maximum change of the magnetization with temperature. With DSC, a pronounced
shift of the signal is observed during cooling or heating at about 1017K and 1037K, respectively. This shift is due to the hysteresis of the DSC method and depends on the temperature gradient $\dot{T}(t)$. The signals are attributed to changes of the magnetic properties, as no structural transitions were observed in this temperature range. Therefore, one expects a mean value of (1030±5)K for the magnetic phase transition of Co$_2$FeSi. The melting point was also observed by DSC and found to be $T_m = (1517 ± 5)$K (not shown in Fig.3).

The observation of the magnetic transition by DSC is verified by the comparison of the structures in DSC with the differential magnetization. The latter is clearly observed at the point of maximum change of the magnetization with temperature. It is seen that the value obtained by DSC is slightly lower than $T_C$ determined from the VSM measurement. For Co$_2$FeSi one finds it to be only 4.5% below the Curie temperature and thus the DSC value may be a simple estimate for $T_C$ if other methods are not available.

III. SUMMARY

The structural and magnetic properties of the Heusler compound Co$_2$FeSi were reported. Co$_2$FeSi has a lattice parameter of 5.64Å and crystallizes in the L2$_1$ structure with very low disorder. Its melting point appears at (1517 ± 5)K. The material is soft magnetic and its specific saturation magnetization of 0.166Am$^2$kg$^{-1}$ at 0K exceeds the one of pure Co by about 9%. The Curie temperature of 1100K is 5% higher than that of pure Fe. The magnetic moment of 6µB per unit cell points clearly on a half-metallic ferromagnet.

As a practical application, it was shown how to estimate the lower temperature limit of the magnetic phase transition for materials with very high Curie temperatures by means of differential scanning calorimetry.

Acknowledgments

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[16] Niculescu et al reported in [12]: $a = 5.66Å$, $T_C > 980$K and $m = 5.9\mu_B$ at 10K; the lattice parameter (5.64Å) found here agrees with the one reported in [12] for Fe$_2$CoSi; Values for $a$ and $m$ reviewed later are considerably different, for unknown reasons.