Investigation of Co$_2$FeSi: The Heusler compound with Highest Curie Temperature and Magnetic Moment.

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Abstract

This work reports on structural and magnetic investigations of the Heusler compound Co$_2$FeSi. X-Ray diffraction and Mößbauer spectrometry indicate an ordered $L_2_1$ structure. Magnetic measurements by means of X-ray magnetic circular dichroism and magnetometry revealed that this compound is, currently, the material with the highest magnetic moment (6$\mu_B$) and Curie-temperature (1100K) in the classes of Heusler compounds as well as half-metallic ferromagnets.

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Materials that exhibit half-metallic ferromagnetism are seen to be potential candidates for the field of application being called spintronics, that is electronics making use of electron spin instead of its charge. The concept of half-metallic ferromagnetism was first presented by de Groot, predicting it to appear in half Heusler compounds. The model suggests that the density of states exhibits, around the Fermi energy ($\epsilon_F$), a gap for minority electrons. Thus, these materials are supposed to be 100% spin polarized at $\epsilon_F$. Most of the predicted half-metallic ferromagnets (HMF) belong to the Heusler compounds. In general, these are ternary $X_2YZ$-compounds crystallizing in the $L2_1$ structure. $X$ and $Y$ are usually transition metals and $Z$ is a main group element.

The Co$_2$ based Heusler compounds exhibit the highest Curie temperature ($T_C = 985K$, Co$_2$MnSi) and the highest magnetic moment (5.54$\mu_B$ per unit cell, Co$_2$FeGe) being reported up to now. High Curie temperatures, magnetic moments, and large minority gaps are desirable for applications. For room temperature devices, in particular, one needs to prevent a reduction of the magnetic properties by thermal effects. The HMF character of Co$_2$MnZ compounds was first reported by Ishida et al. Recently, Co$_2$MnSi and Co$_2$MnGe were used to build first thin film devices. The present work reports on structural and magnetic properties of Co$_2$FeSi.

In the past, this compound was reported to exhibit a magnetic moment of only 5.18$\mu_B$ per unit cell and a Curie temperature of above 980K. One expects, however, that it has a magnetic moment of 6$\mu_B$ if following the rule of thumb ($m = N_V - 24$, where $N_V$ is the number of accumulated valence electrons in the unit cell) based on the Slater Pauling rule.

Co$_2$FeSi samples were prepared by arc-melting of stoichiometric quantities of the constituents in an argon atmosphere. Care was taken to avoid oxygen contamination. Afterwards, the polycrystalline ingots were annealed in an evacuated quartz tube at 1300K for 20 days. This procedure resulted in samples exhibiting the correct Heusler type structure ($L2_1$) as was proved by X-ray diffraction (XRD) using Cu-K$_\alpha$ and Mo-K$_\alpha$ radiation. The lattice constant was determined to be 5.64Å from Rietveld refinement. The $R_{Bragg}$-value was estimated to be $< 5.5$. A disorder between Co and Fe atoms (DO$_3$ type disorder) can be excluded from the XRD Rietveld refinement (see Fig.1) as well as from Neutron scattering data (not shown here). A small disorder between Fe and Si ($B2$ type disorder) atoms ($< 10\%$) can not be excluded from neither of these methods, particularly due to the
FIG. 1: XRD of Co$_2$FeSi.

Shown are the measured intensity ($I_{\text{exp}}$) and the difference to the Rietveldt refinement ($I_{RR}$). Vertical bars indicate the Bragg positions.

low intensities of the (111) and (200) diffraction peaks in XRD. The lattice parameter is obviously smaller than reported [10] and a lower degree of disorder is observed in the present work (compare to Ref. [13]).

For further structural and magnetic investigations, Mößbauer spectroscopy was performed in transmission geometry using a constant acceleration spectrometer with a source line width of 0.105mm/s ($^{57}$Co(Rh)). The observed $^{57}$Fe Mößbauer line width of 0.15mm/s is characteristic for a well-ordered system. The value is comparable to 0.136mm/s observed from $\alpha$-Fe at 4.2K. In detail, the Mößbauer spectrum exhibits a sextett with an isomer shift of 0.23mm/s and a hyperfine magnetic field of $26.3 \times 10^6$A/m at 85K. No quadrupole splitting was detected as expected for the cubic symmetry of the local Fe environment. A $DO_3$ like disorder can be definitely excluded by comparing measured and calculated hyperfine fields in ordered and disordered structures.

Low temperature magnetometry was performed using a super conducting quantum interference device (SQUID) to proof the estimated saturation moment. The results are shown in Fig.2. The measured magnetic moment in saturation is $(5.97 \pm 0.05)\mu_B$ at 5K corresponding to $1.49\mu_B$ per atom. This value is obviously larger than the previously reported $(5.18\mu_B$ see: [10, 13]). An extrapolation to $6\mu_B$ per unit cell at 0K fits perfectly to the moment estimated from the Slater-Pauling rule [11, 12, 14]. The measurement of the magnetic moment reveals, as expected for a HMF, an integer within the experimental uncertainty. Regarding the re-
FIG. 2: Magnetic properties of Co$_2$FeSi.

The field dependence of the magnetic moments was measured by SQUID magnetometry at different temperatures. The inset shows the temperature dependence of the specific magnetization measured by VSM.

As a result of the measurement (an integer) and the rule of thumb, it all sums up to an evidence for half-metallic ferromagnetism in Co$_2$FeSi. In more detail, Co$_2$FeSi turns out to be soft magnetic with a small remanence of $\approx 0.3\%$ of the saturation moment and a small coercive field of $\approx 750\text{A/m}$, under the experimental conditions used here.

The experimental magnetic moment is supported by band structure calculations revealing a HMF character with a magnetic moment of $6\mu_B$. The results of these calculations will be given elsewhere \[15\].

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 taken at the $L_{2,3}$ absorption edges of Fe and Co are shown in Fig.3. The feature seen at 3eV below the $L_3$ absorption edge of Co is related to the $L2_1$ structure and points on the high structural order of the sample (it vanishes for $B2$ like disorder). The magnetic moments per atom derived from a sum rule analysis \[16, 17\] are $(2.6 \pm 0.1)\mu_B$ for Fe and $(1.2 \pm 0.1)\mu_B$ for Co, at 300K and $\mu_0H = 0.4\text{T}$. 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. All values are in good agreement with electronic structure calculations \[15\].

Inspecting the magnetic data of the known Heusler compounds (see data and references
FIG. 3: Site resolved magnetic properties of Co$_2$FeSi.

Shown are the XAS ($I_0$) and XMCD ($I_{MCD}$) spectra taken at the $L_{2,3}$ absorption edges of Fe (a) and Co (b) after subtracting a constant background.

in [18, 19]), one finds a very interesting aspect. Seemingly, a linear dependence (not shown here) is obtained for Co$_2$ based Heusler compounds when plotting the Curie temperature ($T_C$) of the known, 3$d$ metal based Heusler compounds as function of their magnetic moment. According to this plot, $T_C$ is highest for those half-metallic compounds that exhibit a large magnetic moment, or equivalently for those with a high valence electron concentration as derived from the Slater-Pauling rule. $T_C$ is estimated to be above 1000K for compounds with $6\mu_B$ by an extrapolation from the linear dependence.

The high temperature magnetization of Co$_2$FeSi was measured by means of a vibrating sample magnetometer (VSM) equipped with a high temperature stage. The specific magnetization as function of the temperature is shown in the inset of Fig. 2. The measurements were performed in a constant induction field of $\mu_0H = 0.1$T. For this induction field, the specific magnetization at 300K is 37% of the value measured in saturation. The ferromagnetic Curie temperature is found to be $T_C = (1100 \pm 20)$K. This value fits very well to the linear behavior of $T_C$ as a function of valence electrons for Co$_2$ based Heusler compounds as mentioned above. $T_C$ is well below the melting point being obtained by means of differential scanning calorimetry to be $T_m = (1520 \pm 5)$K.

The highest known Curie temperature is reported for elemental Co to be 1388K [20]. Only few materials exhibit a $T_C$ above 1000K, for example the Fe-Co binary alloys. With a value of $\approx 1100$K, Co$_2$FeSi has a higher Curie temperature than Fe and the highest of all
HMF and Heusler compounds being measured up to now.

In summary, the present work shows that $L2_1$ ordered $\text{Co}_2\text{FeSi}$ is a half-metallic ferromagnet exhibiting the highest values for Curie temperature and magnetic moment reported for full Heusler compounds.

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