

Co₂CrIn: A Further Magnetic Heusler Compound

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Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70th birthday

A further example of the class of Heusler compounds is presented. Co₂CrIn is L2₁ ordered (face centered cubic, space group $Fm\bar{3}m$) with a lattice constant of $a = 6.0596(2)$ Å. The crystal structure was determined from powder diffraction data by means of the Rietveld method. The magnetic properties of Co₂CrIn were measured by means of SQUID magnetometry. The material turns out to be a soft ferromagnet with a saturation moment of $1.2 \mu_B$ at 5 K.

Key words: Magnetic Properties, Heusler Compounds

Introduction

The Co₂YZ Heusler compounds (with Y = transition metal and Z = main group metal) exhibit the highest Curie temperatures (1100 K, Co₂FeSi [1–3] and the highest magnetic moments ($6.0 \mu_B$ per unit cell, Co₂FeSi [1–3]) being reported up to now.

In particular, some Co₂CrZ Heusler compounds with Z = (Al, Ga) are reported to be half-metallic ferromagnets [4–8]. The magnetic moment of Co₂CrGa is reported by Umetsu *et al.* [9] to be $3.01 \mu_B$ [9]. This value is in accordance with the Slater-Pauling rule. In particular, the measured magnetic moment is an integer value, which points to a half-metallic character for Co₂CrGa. Co₂CrAl is also predicted to be a half-metallic ferromagnet. In experiments, however the compound reveals a magnetic moment of only $1.55 \mu_B$ [10]. This value is half of the value obtained from the Slater-Pauling rule [11–13] and is no integer value.

The quaternary Heusler compounds Co₂Cr_{1-x}Fe_xAl show also magnetic moments, which are significantly lower in bulk materials [4–8, 10, 14, 15] and in tunnel junctions [16–19] compared to the value [11–13] expected from the Slater-Pauling rule.

This reduction of the magnetic moment might originate from an interchange of Cr and Co sites, as proposed by Miura *et al.* [6, 7]. This type of disorder leads to an antiferromagnetic coupling of the antisite-Cr with the nearest neighbour ordinary site-Cr atoms and de-

grades the half-metallic character. Zhang *et al.* [15] estimated the Co-(Cr,Fe) (DO₃ type) disorder to be about 30%. X-ray magnetic circular dichroism measurements of Co₂Cr_{1-x}Fe_xAl revealed that the measured site specific moment of the Cr is significantly smaller than the calculated value. This points to disorder effects and selective oxidation of Cr [20, 21]. The site specific results are in agreement with measurements of the total moments as mentioned above.

Nevertheless, pressed powder samples of Co₂Cr_{0.6}-Fe_{0.4}Al show a very high magnetoresistance ratio (30%) at room temperature [4, 5] in bulk material and large tunneling magnetoresistance between 19% [16–18] and 42% [19, 22] in tunnel junctions. The equi-electronic Co₂Cr_{1-x}Fe_xGa compounds crystallise in the ordered L2₁ structure and the magnetic moments for the compounds with low concentration of x are in good agreement with the Slater Pauling rule [23, 24].

A comprehensive characterisation of Cr containing Heusler compounds is necessary in order to understand the mechanism of the reduced magnetic moment of Cr in the Co₂Cr_{1-x}Fe_xAl compounds in contrast to the Co₂Cr_{1-x}Fe_xGa compounds. While Co₂YZ Heusler compounds with Z = Al, Ga are already known, the next compound with an element of the series of main group elements is a Co₂YZ Heusler compound with Z = In. This compound has not been reported up to now. Therefore (see Fig. 1) Co₂CrIn was synthesised and characterised in the present study.

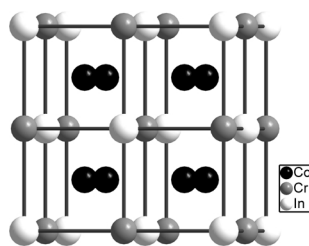


Fig. 1. Crystal structure of Co₂CrIn.

Experimental Section

Polycrystalline samples of Co₂CrIn were prepared by repeated arc-melting of stoichiometric quantities of the pure metals in a purified argon atmosphere. The weight loss was monitored to be less than 0.5%.

The Heusler type (L2₁) structure was determined by X-Ray powder diffraction (Bruker AXS D8) with a mixture of Cu-K_{α1} and Cu-K_{α2}-radiation. The measurements were performed in reflection geometry in a θ - θ scanning mode. A multilayer Göbel mirror was used as monochromator. The 2θ scan range was set from 15° to 115.106° with a step size of 0.0357° leading to 2804 independent measurement points. All measurements were performed at room temperature. The structural parameters of Co₂CrIn were obtained from refinement of the XRD data using the Jana2000 program package [25].

The magnetic properties were investigated at low temperatures using a superconducting quantum interference device (SQUID, Quantum Design MPMS-XL-5).

Results and Discussion

Heusler compounds [26] are ternary intermetallics with stoichiometric composition X_2YZ . Fig. 2 shows the diffractogram of Co₂CrIn. The data was refined in the face centered cubic Heusler type L2₁ structure (BiF₃ type) [27]. A scheme of the Heusler type structure can be seen in Fig. 1. All reflections of Co₂CrIn were identified using the space group $Fm\bar{3}m$, number 225. The Co atoms are located on the 8c Wyckoff position ($1/4, 1/4, 1/4$), the Cr atoms on 4b ($1/2, 1/2, 1/2$) and In on 4a (0 0 0). There are 4 formula units per unit cell leading to an overall composition of Co₈Cr₄In₄. The background was refined using 9 terms of a Legendre Polynom and the 2θ -range of 15°–22° was excluded from the refinement. Within the fitting procedure, the peak form was assumed to have a Lorentz-shape with $L_x = 8.2(5)$ and $L_y = 21.5(13)$.

The lattice constant is determined with this refinement parameter to be 6.0596(2) Å. The positional and atomic displacement factors U_{iso} are small with U_{iso} (Co) = 0.019(2), U_{iso} (Cr) = 0.027(2) and U_{iso} (In) =

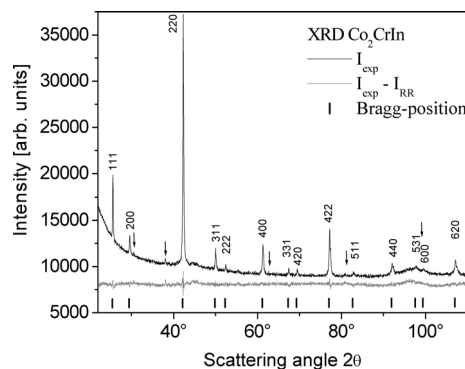


Fig. 2. Diffraction pattern and difference plot of the Rietveld refinement of Co₂CrIn. Shown are the measured intensity (I_{exp}) and the difference compared to the Rietveld refinement (I_{RR}). Vertical bars indicate the Bragg positions of the expected diffraction peaks. Reflections of a secondary phase, which could not be identified, are marked with arrows.

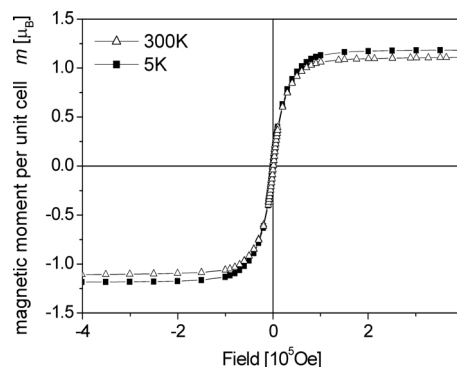


Fig. 3. Magnetic hysteresis curve of Co₂CrIn at 5 K and 300 K, respectively.

0.007(2). The cell volume is 222.506(8) Å³ and the calculated density amounts to 8.495(3) g/cm³.

The quality of the fit was denoted in the values of $R = 3.59$, $R_{wobs} = 1.5$ and $R_{wall} = 1.54$. In addition, the diffractogram of Co₂CrIn exhibits additional reflections due to a small amount of an unidentified phase. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), depository number CSD-416260.

The refinement of Co₂CrIn revealed no large disorder effects in contrast to Co₂CrAl. A high degree of disorder arising from the Co and Cr positions (DO₃ disorder) could be excluded from the refinement. Any disorder influences the intensities of the (111) and (200) reflection. Thus the ratio of the intensities of the (111) and (200) reflection might be used as an indica-

tor of disorder effects in this class of compounds. In Co₂CrIn, the cross sections of Cr and In are of different orders of magnitude in contrast to Cr and Ga. Thus the ratio of the intensities of the (111) and (200) reflections of Co₂CrIn is more significant in Co₂CrIn than in Co₂CrGa and Co₂CrAl and disorder effects are more apparent.

The magnetic properties were measured by means of SQUID magnetometry. Fig. 3 shows the hysteresis curves of Co₂CrIn measured at 5 K and 300 K. The magnetic moment in saturation is 1.18 μ_B at 5 K and 1.1 μ_B at 300 K corresponding to a magnetic moment of 0.3 μ_B per atom at 5 K and 0.28 μ_B per atom at 300 K, respectively. Co₂CrIn turns out to be a soft ferromagnet with a small remanence and a small coercive field.

Many Co₂YZ Heusler compounds follow the Slater-Pauling curve [11,12], as described by Kübler [13]. An application of this *valence electron rule* on Co₂CrIn leads to a magnetic moment of 3 μ_B . This is the expected magnetic moment for all Co₂CrZ compound with Z being a third main group element, if the compound is predicted to be a half-metallic ferromagnet. Thus the measurement reveals a reduced magnetic mo-

ment and excludes half-metallic ferromagnetic ordering. The structural refinement showed no major disorder. Therefore the reduced magnetic moment is not due to disorder effects and may arise from a ferri – or an antiferromagnetic coupling of the Co and Cr atoms.

Summary and Outlook

In summary, this work presents the synthesis and characterisation of the Heusler compound Co₂CrIn. The compound is L2₁ ordered and shows no major antisite disorder. Co₂CrIn turns out to be a ferrimagnet with a magnetic moment of 1.18 μ_B at 5 K. In addition, the hysteresis curve reveals a soft magnetic behaviour. A measurement of the site specific magnetic moments is highly desirable as it might lead to a deeper understanding of the magnetic properties of Co₂CrIn. Furthermore, the measured magnetic moment is not an integer number, as expected for a half-metallic ferromagnet. Thus, Co₂CrIn can not be a half-metallic ferromagnet, as most of the other Co₂YZ Heusler compounds.

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