Co_2CrIn: 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. Co_2CrIn is $L2_1$ 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 Co_2CrIn were measured by means of SQUID magnetometry. The material turns out to be a soft ferromagnet with a saturation moment of 1.2 μ_B at 5 K.

Key words: Magnetic Properties, Heusler Compounds

Introduction

The Co_2YZ Heusler compounds (with Y = transition metal and Z = main group metal) exhibit the highest Curie temperatures (1100 K, Co_2FeSi [1 – 3] and the highest magnetic moments (6.0 μ_B per unit cell, Co_2FeSi [1 – 3]) being reported up to now.

In particular, some Co_2CrZ Heusler compounds with Z = (Al, Ga) are reported to be half-metallic ferromagnets [4 – 8]. The magnetic moment of Co_2CrGa is reported by Umetsu *et al.* [9] to be 3.01 μ_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 Co_2CrGa. Co_2CrAl is also predicted to be a half-metallic ferromagnet. In experiments, however the compound reveals a magnetic moment of only 1.55 μ_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 $Co_2Cr_{1-x}Fe_xAl$ 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 degrades the half-metallic character. Zhang *et al.* [15] estimated the Co-(Cr,Fe) (DO_3 type) disorder to be about 30%. X-ray magnetic circular dichroism measurements of $Co_2Cr_{1-x}Fe_xAl$ 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 $Co_2Cr_{0.6}Fe_{0.4}Al$ 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 $Co_2Cr_{1-x}Fe_xGa$ compounds crystallise in the ordered $L2_1$ 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 $Co_2Cr_{1-x}Fe_xAl$ compounds in contrast to the $Co_2Cr_{1-x}Fe_xGa$ compounds. While Co_2YZ Heusler compounds with Z = Al, Ga are already known, the next compound with an element of the series of main group elements is a Co_2YZ Heusler compound with Z = In. This compound has not been reported up to now. Therefore (see Fig. 1) Co_2CrIn was synthesised and characterised in the present study.

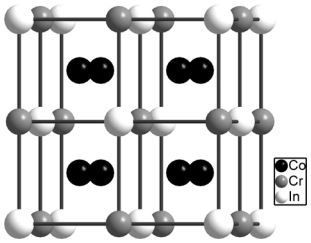

Fig. 1. Crystal structure of Co_2CrIn.

Experimental Section

Polycristalline samples of Co_2CrIn 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 ($L2_1$) structure was determined by X-Ray powder diffraction (Bruker AXS D8) with a mixture of Cu-$K_{\alpha 1}$ and Cu-$K_{\alpha 2}$-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 Co_2CrIn were obtained from refinement of the XRD data using the Jana2000 program package [25].

The magnetic properties were investigated at low temperatures using a super conducting 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 Co_2CrIn. The data was refined in the face centered cubic Heusler type $L2_1$ structure (BiF_3 typ) [27]. A scheme of the Heusler type structure can be seen in Fig. 1. All reflections of Co_2CrIn were identified using the space group $Fm\bar{3}m$, number 225. The Co atoms are located on the 8*c* Wykhoff position ($1/4\ 1/4\ 1/4$), the Cr atoms on 4*b* ($1/2\ 1/2\ 1/2$) and In on 4*a* (0 0 0). There are 4 formular units per unit cell leading to an overall composition of $Co_8Cr_4In_4$. 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) $=$ $0.007(2)$. The cell volume is 222.506(8) $Å^3$ and the calculated density amounts to 8.495(3) g/cm^3.

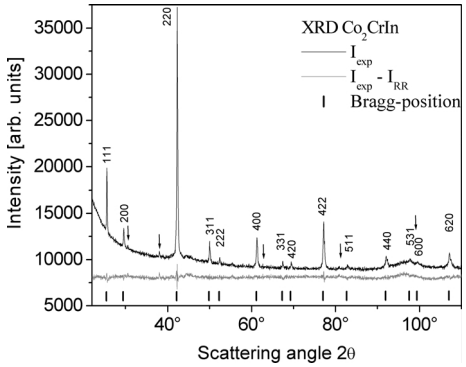

Fig. 2. Diffraction pattern and difference plot of the Rietveld refinement of Co_2CrIn. Shown are the measured intensity (I_{exp}) and the difference compared to the Rietveld refinement (I_{RR}). Vertical bars indicate the Bragg positions of the expected diffraction peaks. Reflections of a secondary phase, which could not be identified, are marked with arrows.

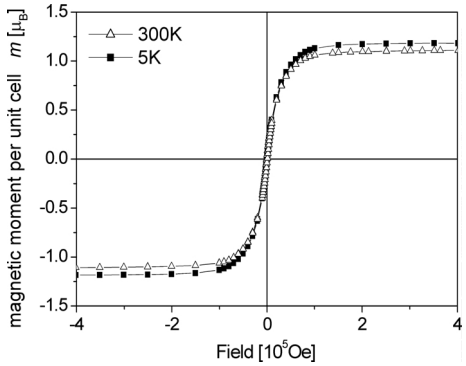

Fig. 3. Magnetic hysteresis curve of Co_2CrIn at 5 K and 300 K, respectively.

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 Co_2CrIn 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 Co_2CrIn revealed no large disorder effects in contrast to Co_2CrAl. A high degree of disorder arising from the Co and Cr positions (DO_3 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 Co_2CrIn, 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 Co_2CrIn is more significant in Co_2CrIn than in Co_2CrGa and Co_2CrAl and disorder effects are more apparent.

The magnetic properties were measured by means of SQUID magnetometry. Fig. 3 shows the hysteresis curves of Co_2CrIn 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. Co_2CrIn turns out to be a soft ferromagnet with a small remanence and a small coercive field.

Many Co_2YZ Heusler compounds follow the Slater-Pauling curve [11,12], as described by Kübler [13]. An application of this *valence electron rule* on Co_2CrIn leads to a magnetic moment of 3 μ_B. This is the expected magnetic moment for all Co_2CrZ 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 moment 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 Co_2CrIn. The compound is $L2_1$ ordered and shows no major antisite disorder. Co_2CrIn turns out to be a ferrimagnet with a magnetic moment of 1.18 μ_B at 5 K. In addition, the hysterisis 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 Co_2CrIn. Furthermore, the measured magnetic moment is not an integer number, as expected for a half-metallic ferromagnet. Thus, Co_2CrIn can not be a half-metallic ferromagnet, as most of the other Co_2YZ Heusler compounds.

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