Structure and magnetism of Co$_2$CrAl Heusler alloy films*

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We report on magnetic properties of Co$_2$CrAl thin films. Low-field magnetization measurements show that the films with the best $B_2/L_21$ structure exhibit ferromagnetic order below the Curie temperature $T_C \approx 330–340$ K and below 200 K they exhibit magnetic characteristics suggesting the presence of antiferromagnetic ordering. Our ferromagnetic resonance measurements confirm a complex magnetic phase diagram of Co$_2$CrAl due to a disorder between Co and Cr sites in nominally $L2_1$ or $B2$ structures.

Key words: magnetic properties; Co$_2$CrAl thin film; Heusler alloy

1. Introduction

Heusler alloys (HA) have attracted scientific and technological interest for their potential use as materials for spintronic devices since some of them are half-metallic ferromagnets, i.e., they exhibit a complete spin polarization at the Fermi level. For example, Ishida et al. [1] have shown that Co$_2$CrAl HA has a complete spin polarization at the Fermi level. Later on, Galanakis [2] predicted that Co$_2$CrAl may preserve nearly half-metallic behaviour even at the surface, which in most HA can be regarded as a two-dimensional defect. In HA, the defects (atomic disorder, for example) are known to substantially deteriorate half-metallicity. In Co$_2$CrAl, it has been found [3] that Co/Cr type of atomic disorder destroys spin polarization while Cr/Al disorder does not significantly influence its half-metallicity.

Co$_2$CrAl HA can be regarded as the end-point of a series of Co$_2$Cr$_{1-x}$Fe$_x$Al (further referred to as CCFA) which have recently received much attention for their remarkable


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magnetoresistive properties found in pressed powder compacts [4]. Thin CCFA films have been extensively investigated in the context of potential applications in spintronic devices, too. Inomata et al. [6] have shown that a magnetic tunnelling junction based on the Heusler alloy Co$_2$Cr$_{0.6}$Fe$_{0.4}$Al with a disordered $B_2$ structure has a relatively large tunnel magnetoresistance of 16% at RT and $-26.5\%$ at 5 K. Hirohata et al. [8] reported on deposition of Co$_2$CrAl films on GaAs substrates by using MBE in a UHV environment. They have shown that the Co$_2$CrAl films have a mixed $L2_1/B2$ (or even $A2$) structure.

Even though the CCFA HA hold a promise for the realization of half-metallicity at RT, their magnetic properties have been found to largely differ from the theoretically predicted [2] for the $L2_1$ structure ($\sim 3\mu_B$ per formula unit $= 600 \text{ G}$), where the magnetic moments of Co and Cr are 0.76 and 1.54$\mu_B$, respectively. For example, the magnetic moment per formula unit at 5 K has been estimated to $\sim 0.9\mu_B$ for Co$_2$CrAl thin films with $B2$ structure [6]. It is significantly lower than $\sim 1.7\mu_B$ reported for a polycrystalline bulk alloy [9] with $A2$ structure and about 3 times lower than the theoretical value. Generally, the same as in other HA, it has been found that the magnetic properties (the Curie temperature and the saturation magnetization) of Co$_2$CrAl are strongly depressed due to disorder and inhomogeneities at the micrometric level and depends on the method of synthesis [4]. In this paper, we study magnetic properties of polycrystalline Co$_2$CrAl thin films with various structural ordering. We show that, depending on the ordering, low temperature magnetic properties and the Curie temperature of Co$_2$CrAl thin films may vary substantially.

2. Experimental details

Bulk Co$_2$CrAl HA was prepared by melting Co, Cr and Al pieces of 99.99% purity together in an arc furnace with a water-cooled Cu hearth under Ar atmosphere at the pressure of 1.3 atm. To promote the volume homogeneity, the ingot was remelted 5 times and then annealed at 1273 K during 10 h under vacuum. The X-ray fluorescence analysis revealed the alloy composition of Co$_{0.517}$Cr$_{0.245}$Al$_{0.238}$ (hereafter referred to as Co$_2$CrAl). Co$_2$CrAl alloy films about 100 nm thick with various degrees of the structural order were prepared by flash evaporation onto glass and NaCl substrates simultaneously under vacuum better than $2\times10^{-5} \text{ Pa}$. To obtain the Co$_2$CrAl films with the maximum possible disorder, we deposited them onto substrates cooled by liquid nitrogen ($T_s \approx 150 \text{ K}$). Such as-deposited Co$_2$CrAl films were then subsequently annealed at 538, 608 and 760 K for 1 h under high vacuum. Additionally, some Co$_2$CrAl films were also deposited onto substrates at 723 K. The Co$_2$CrAl alloy films with various structural order are referred as the films in states 1 ($T_s \approx 150 \text{ K}$), 2 ($T_{\text{ann}} = 538 \text{ K}$), 3 ($T_{\text{ann}} = 608 \text{ K}$), 4 ($T_{\text{ann}} = 760 \text{ K}$) and 5 ($T_s = 723 \text{ K}$), respectively (see Table 1). The structural characterization of the samples was carried out by selective-area microdiffraction of transmission electron microscopy (TEM) for the films deposited and separated from the NaCl substrates. The structural properties of Co$_2$CrAl films are summarized in Table 1.
3. Results and discussion

A standard method applied to order structurally HA films is their annealing at elevated temperatures [7] or deposition onto heated substrates [8]. Figure 1 shows TEM diffractograms and dark field TEM images of the Co2CrAl films deposited onto substrates cooled at 150 K (Fig. 1a – state 1) and subsequently annealed at 538 K (Fig. 1b – state 2), 608 K (Fig. 1c – state 3) and 760 K (Fig. 1d – state 4), respectively.

The films in state 1 are nanocrystalline or amorphous. Annealing at 538 K results in their crystallization with A2 type of ordering and a very small grain size of 10 nm. Annealing at higher temperatures (Figs. 1c, d) leads not only to a further increase of
structural order to $B_2$ ($T_{\text{ann}} = 608$ K) or a mixed $B_2/L_21$ ($T_{\text{ann}} = 760$ K) structure but also to a significant grain size growth up to 1000 nm.

Such a large growth in structural order brings about a growth in ferromagnetic ordering. As can be seen in Table 1, both the Curie temperature $T_C$ and the saturation magnetization $M_S$ increase with the growth in structural ordering. But even the best-ordered Co$_2$CrAl films (state 4) have magnetization much lower than theoretically predicted $M_S = 600$ G [2].

![Magnetization measured at 175 K and 293 K as a function of magnetic field for $B_2/L_21$ ordered Co$_2$CrAl film annealed at 760 K (state 4)](image)

Figure 2 shows the hysteresis loops of the Co$_2$CrAl film in state 4 recorded at 175 and 293 K, respectively. The saturation magnetization at 175 K is only 350 G what gives $1.7\mu_B$ per formula unit. Similar results have been reported by Inomata et al. [6]. In state 4 the Co$_2$CrAl film is a soft magnet: its coercivity $H_C$ is 80 Oe at 175 K, decreasing to 30 Oe at 293 K. Nevertheless, despite low coercivity, the magnetization at 175 K saturates at relatively high fields of the order of 2–3 kOe, suggesting the existence of local antiferromagnetic (AF) interactions at low temperatures even in the best-ordered films. This may be attributed to Cr atoms partially occupying Co sites, as was theoretically suggested by Miura et al. [3], who have shown that Cr atoms occupying Co sites are antiferromagnetically coupled with Co atoms. To check such a scenario, we measured the temperature dependence of the magnetic moment in a low external magnetic field of 100 Oe in a zero-field-cooled state (ZFC) by cooling it from 350 K to 5 K in the absence of magnetic field. Subsequently, magnetic field was applied and the measurements were taken on increasing temperature up to 350 K. Then, without removing the external field, the measurement was made on decreasing temperature, i.e., in a field-cooled (FC) state. Figure 3 shows the results of ZFC and FC
measurements for the Co₂CrAl film in state 4. It is seen that ZFC curve does not re-
trace the FC curve in a similar way as in the magnetic materials with competing F/AF
interactions (e.g., spin glasses). In our best-ordered Co₂CrAl films, such a behaviour
would be rather explained as resulting from coexistence of AF exchange within ferro-
magnetic matrix. The nature of the onset of AF ordering in Co₂CrAl films at low tem-
peratures is not clear at present: it can either arise from a structural martensitic trans-
formation (as in some HA, for example Ni–Mn–Sn HA [10]) or it is just related to a
local AF exchange leading to non-collinear spin structures which can pin the ferro-
magnetic domains in different configuration depending on whether the sample is
cooled in an external field or not. The Curie temperature \( T_C \) estimated from the low-
field magnetization measurements is 340 K.

![FC (solid symbols) and ZFC (open symbols) \( M(T) \) dependences](image)

The anomalous ZFC characteristics for the best ordered Co₂CrAl film with \( B2/L2_1 \)
structure is confirmed by the FMR results. Figure 4a shows the temperature depend-
ence of the effective magnetization \( 4\pi M_{\text{eff}} \) for the film in the state 4 and 3, for com-
parison. \( 4\pi M_{\text{eff}} = H_{\text{epp}}^{\text{perf}} - \omega / \gamma \) was calculated from the resonance field \( H_{\text{epp}}^{\text{perf}} \) measured
in the perpendicular configuration assuming g-factor equal 2.1, i.e., the same as for
other HA [11]. It is seen that \( 4\pi M_{\text{eff}} \) of the Co₂CrAl film in state 4 experiences a simi-
lar anomalous behaviour as ZFC magnetization, i.e., it decreases substantially below
200 K. If the temperature behaviour of \( 4\pi M_{\text{eff}} \) were regular (as is shown in Fig. 4a by
a dashed curve), the extrapolated to 0 K \( 4\pi M_{\text{eff}} \) value would attain \( \sim 5200 \) G (\( M_{\text{eff}} \)
\( \approx 400 \) G) in a rough agreement with our static magnetization data (Fig. 2). On the
other hand, \( 4\pi M_{\text{eff}} \) vs. \( T \) for the film in state 3 is quite regular with the value extrapo-
lated to 0 K of the order of 4000 G (\( M_{\text{eff}} \approx 320 \) G). The estimated \( T_C \) for the film in state
3 is of \( \sim 290 \) K in agreement with the low-field magnetization data. However, for the
film in state 4 the FMR signal is observed at temperatures higher than \( T_C = 340 \) K.
would indicate the existence of the local ferromagnetic correlations well above $T_C$ in the Co$_2$CrAl films with the highest structural ordering. We argue that the Co/Cr antitsite disorder seems to be responsible for these high-temperature ferromagnetic correlations. According to the theoretical calculations [12], the Cr magnetic moment strongly depends not only on the kind of surrounding atoms but also on the arrangement of these atoms around the Cr atom. Hence, both anomalous behaviour of $4\pi M_{\text{eff}}$ at low temperatures due to mixed ferro-/antiferromagnetic exchange and the high-temperature correlations above $T_C$ may be regarded as the experimental evidences of a local structural disorder of Co and Cr atoms.

![Image](image_url)

**Fig. 4.** Temperature dependences of the effective magnetization $4\pi M_{\text{eff}}$ of the Co$_2$CrAl films annealed at 608 K (state 3) and 760 K (state 4) (a); FMR resonance linewidth $\Delta H$ for the same films (b)

FMR linewidth $\Delta H$ is a sensitive measure of the presence of magnetic inhomogeneities in magnetic thin films [13]. Inhomogeneties of the internal effective magnetic field lead to an inhomogeneous broadening of the FMR linewidth. Therefore, the presence of the low temperature transformation to a mixed ferro-/antiferromagnetic state should perturb the temperature behaviour of $\Delta H$ in Co$_2$CrAl films at low temperatures.
Fig. 4 (b) shows the temperature dependencies of $\Delta H$ measured for the films in state 3 and 4, respectively. It is seen that $\Delta H$ for the film in state 3 is relatively large and increases monotonically on approaching $T_c$ due to the presence of critical correlations near the phase transformation and significant magnetic inhomogeneities [13]. For the film in state 4 the linewidth is very narrow (~90 Oe) and nearly independent of temperature in a range of $175<T<275$ K indicating a very good film quality. However, at low temperatures below ~175 K, it strongly increases. We attribute such an increase to the presence of a mixed ferro-/antiferromagnetic mixed state.

4. Summary

The structure, microstructure and magnetic properties of Co$_2$CrAl thin films were investigated. The best-ordered Co$_2$CrAl films annealed at $T_{\text{ann}} > 700$ K reveal a mixed $B2/L2_1$ structure and the saturation magnetization (extrapolated to 0 K) of 400 G ($\sim 2\mu_B$ per formula unit). The presence of anomalous behaviour in low-field magnetization and FMR response below 175 K can be accounted to the disorder between Co and Cr sites, which makes a considerable reduction of the total magnetic moment per formula unit and the presence of a mixed ferro-/antiferromagnetic exchange coupling.

References


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