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Structure and magnetism of Co_2CrAl Heusler alloy films[*]

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We report on magnetic properties of Co_2CrAl 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_2CrAl due to a disorder between Co and Cr sites in nominally $L2_1$ or *B*2 structures.

Key words: *magnetic properties; Co_2CrAl 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_2CrAl HA has a complete spin polarization at the Fermi level. Later on, Galanakis [2] predicted that Co_2CrAl 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_2CrAl, 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_2CrAl HA can be regarded as the end-point of a series of $Co_2Cr_{1-x}Fe_xAl$ (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 $Co_2Cr_{0.6}Fe_{0.4}Al$ 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_2CrAl films on GaAs substrates by using MBE in a UHV environment. They have shown that the Co_2CrAl films have a mixed $L2_1/B2$ (or even *A*2) 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 (~ $3\mu_B$ per formula unit ≈ 600 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 ~ $0.9\mu_B$ for Co_2CrAl thin films with *B*2 structure [6]. It is significantly lower than ~ $1.7\mu_B$ reported for a polycrystalline bulk alloy [9] with *A*2 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_2CrAl 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_2CrAl thin films with various structural ordering. We show that, depending on the ordering, low temperature magnetic properties and the Curie temperature of Co_2CrAl thin films may vary substantially.

2. Experimental details

Bulk Co_2CrAl 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_2CrAl). Co_2CrAl 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 2×10^{-5} Pa. To obtain the Co_2CrAl films with the maximum possible disorder, we deposited them onto substrates cooled by liquid nitrogen ($T_s \approx 150$ K). Such as-deposited Co_2CrAl films were then subsequently annealed at 538, 608 and 760 K for 1 h under high vacuum. Additionally, some Co_2CrAl films were also deposited onto substrates at 723 K. The Co_2CrAl alloy films with various structural order are referred as the films in states 1 ($T_s \approx 150$ K), 2 ($T_{ann} = 538$ K), 3 ($T_{ann} = 608$ K), 4 ($T_{ann} = 760$ K) and 5 ($T_s = 723$ 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_2CrAl films are summarized in Table 1.

Table 1. Structure, microstructure and magnetic properties of the Co_2CrAl films in various structural states depending on the annealing temperature (T_{ann}) or the substrate temperature (T_s). T_C is the Curie temperature, M_S – saturation magnetization at RT. NM – nonferromagnetic

Film state	T_s [K]	T_{ann} [K]	Lattice parameter [nm]	Structure	Mean grain size [nm]	T_C [K]	M_S [emu/cm^3]
1	150	293	0.578	amorphous	< 2	NM	NM
2	150	538	0.572	*A*2	~ 10	270	NM
3	150	608	0.572	*B*2	~ 1000	290	90
4	150	760	0.570	*B*2/L2_1	~ 1000	340	200
5	728		0.570	*B*2	~ 20- 30	330	220

Magnetic properties were investigated in the temperature range 5–350 K using SQUID magnetometer at low external magnetic field of 100 Oe. The temperature dependences of the out-of-plane ferromagnetic resonance (FMR) at 9.3 GHz were investigated in 80–350 K temperature range. The hysteresis loops were measured with a vibrating sample magnetometer at RT and 175 K.

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 Co_2Cr Al 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.

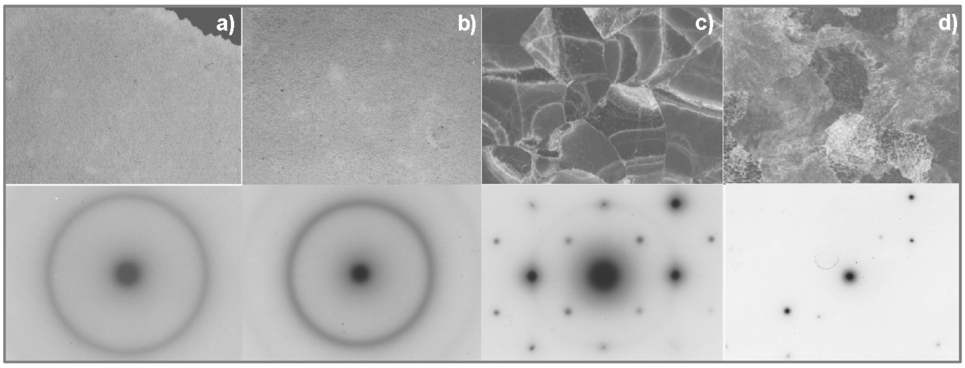

Fig. 1. Room temperature TEM micrographs and diffraction patterns for the Co_2CrAl films deposited onto NaCl substrates at 150 K (a), annealed at 538 K (b), 608 K (c) and 760 K (d)

The films in state 1 are nanocrystalline or amorphous. Annealing at 538 K results in their crystallization with *A*2 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 $B2$ (T_{ann} = 608 K) or a mixed $B2/L2_1$ (T_{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_2CrAl films (state 4) have magnetization much lower than theoretically predicted M_S = 600 G [2].

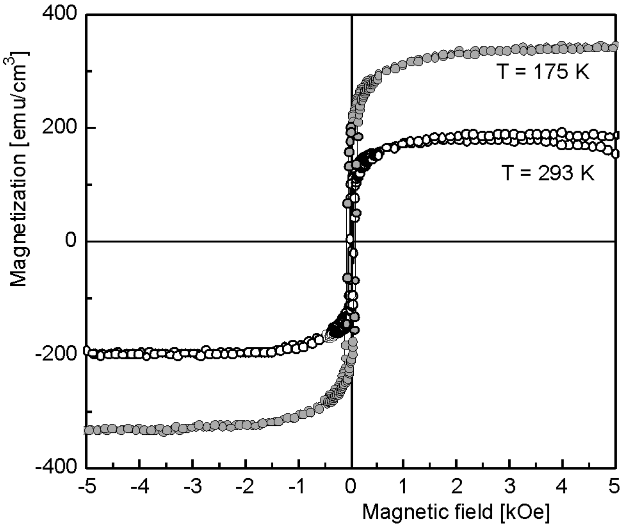

Fig. 2. Magnetization measured at 175 K and 293 K as a function of magnetic field for $B2/L2_1$ ordered Co_2CrAl film annealed at 760 K (state 4)

Figure 2 shows the hysteresis loops of the Co_2CrAl film in state 4 recorded at 175 and 293 K, respectively. The saturation magnetization at 175 K is only 350 G what gives 1.7μ_B per formula unit. Similar results have been reported by Inomata et al. [6]. In state 4 the Co_2CrAl 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 Co_2CrAl film in state 4. It is seen that ZFC curve does not retrace 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 Co_2CrAl films, such a behaviour would be rather explained as resulting from coexistence of AF exchange within ferromagnetic matrix. The nature of the onset of AF ordering in Co_2CrAl films at low temperatures is not clear at present: it can either arise from a structural martensitic transformation (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 ferromagnetic 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.

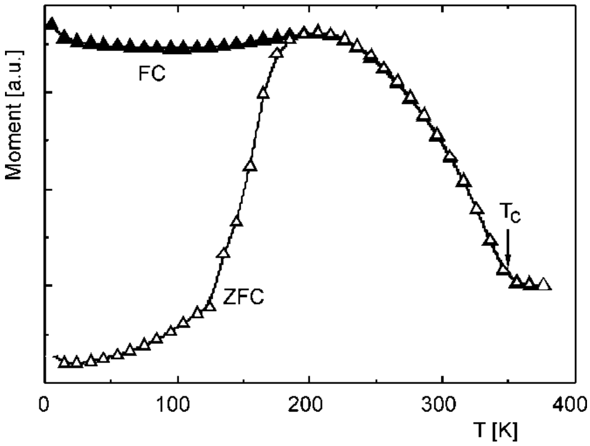

Fig. 3. FC (solid symbols) and ZFC (open symbols) $M(T)$ dependences for the $B2/L2_1$ ordered Co_2CrAl film annealed at 760 K (state 4)

The anomalous ZFC characteristics for the best ordered Co_2CrAl film with $B2/L2_1$ structure is confirmed by the FMR results. Figure 4a shows the temperature dependence of the effective magnetization $4\pi M_{eff}$ for the film in the state 4 and 3, for comparison. $4\pi M_{eff} = H_r^{perp} - \omega/\gamma$ was calculated from the resonance field H_r^{perp} measured in the perpendicular configuration assuming g-factor equal 2.1, i.e., the same as for other HA [11]. It is seen that $4\pi M_{eff}$ of the Co_2CrAl film in state 4 experiences a similar anomalous behaviour as ZFC magnetization, i.e., it decreases substantially below 200 K. If the temperature behaviour of $4\pi M_{eff}$ were regular (as is shown in Fig. 4a by a dashed curve), the extrapolated to 0 K $4\pi M_{eff}$ value would attain ~5200 G (M_{eff} ≈ 400 G) in a rough agreement with our static magnetization data (Fig. 2). On the other hand, $4\pi M_{eff}$ vs. T for the film in state 3 is quite regular with the value extrapolated to 0 K of the order of 4000 G (M_{eff}≈320 G). The estimated T_C for the film in state 3 is of ~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. It would indicate the existence of the local ferromagnetic correlations well above T_C in the Co_2CrAl films with the highest structural ordering. We argue that the Co/Cr antisite 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 $4\pi M_{eff}$ 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.

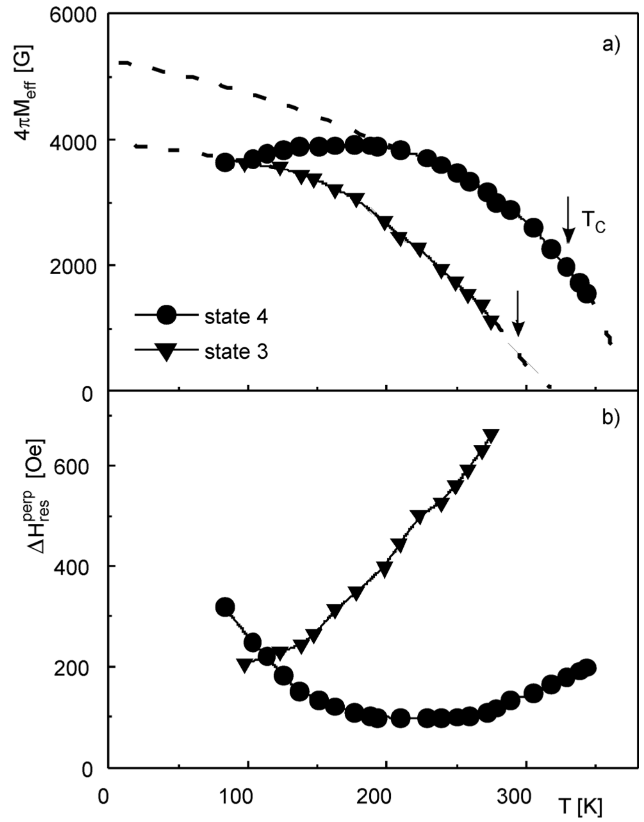

Fig. 4. Temperature dependences of the effective magnetization $4\pi M_{eff}$ of the Co_2CrAl films annealed at 608 K (state 3) and 760 K (state 4) (a); FMR resonance linewidth ΔH for the same films (b)

FMR linewidth ΔH is a sensitive measure of the presence of magnetic inhomogeneities in magnetic thin films [13]. Inhomogenetities 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 ΔH in Co_2CrAl films at low temperatures.

Fig. 4 (b) shows the temperature dependencies of ΔH measured for the films in state 3 and 4, respectively. It is seen that ΔH 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_2CrAl thin films were investigated. The best-ordered Co_2CrAl films annealed at $T_{ann}>700$ K reveal a mixed $B2/L2_1$ structure and the saturation magnetization (extrapolated to 0 K) of 400 G (~$2\mu_B$ 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

[1] ISHIDA S., FUJII S., KASHAWAGI S., ASANO S., J. Phys. Soc. Jpn., 64 (1995), 2152.
[2] GALANAKIS I., J. Phys.: Condens. Matter, 14 (2002), 6329.
[3] MIURA Y., NAGAO K., SHIRAI M., Phys. Rev. B, 69 (2004), 14413.
[4] DE TERESA J.M., SERRATE D., CORDOBA R., YUSUF S.M., to be published in J. Alloys Compd. (2006), doi :10.1016/j.allcom.2006.10.104.
[5] FELSER C., HETKAMP B., KRONAST F., SCHMITZ D., CRAMM S., ELMERS H-J., FECHER G.H., WURMEL S., BLOCK T., VALDAITSEV D., NEPIJKO S.A., GLOSKOVSKII A., JAKOB G., SHÖNHESSE G., EBERHARDT W., J. Phys.: Condens. Matter, 15 (2003), 7019.
[6] INOMATA K., TEZUKA N., OKAMURA S., KUREBAYASHI H., HIROKATA A., J. Appl. Phys., 95 (2004), 7234.
[7] KUDRYAVTSEV Y.V., OKSENENKO V.O., LEE N.N., LEE Y.P., RHEE J.Y., DUBOWIK J., J. Appl. Phys., 97 (2005), 113903.
[8] HIROHATA A., OKAMURA H.S., KIKUCHI M., MASAKI T., NOZAKI T., TEZUKA N., INOMATA K., J. Appl. Phys., 97 (2005), 10C308.
[9] ZHANG M., WOLF A.L., ZHANG L., TEQUS O., BRÜCKE E., WU G., DE BOER F.R., J. Appl. Phys., 97 (2005), 10C301.
[10] KRENKE T., ACET M., WASSERMANN E.F., MOYA X., MAÑOSA L., PLANES A., Phys. Rev. B, 72 (2005), 014412.
[11] PECHAN M.J., YU C., CARR D., PALMSTRÖM C.J., J. Magn. Magn. Mater., 286 (2005), 340.
[12] ANTONOV V.N., DÜRR H.A., KUCHERENKO YU., BEKENOV L.V., YARESKO A.N., Phys. Rev. B, 72 (2005), 054441.
[13] FARLE M., Rep. Prog. Phys., 61 (1998), 755.

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