Structural and Magnetic Properties of the Half-Ferromagnetic $Co_{2+x+y}Mn_{1-x}Al_{1-y}$ Alloys

C. Paduani, A. Migliavacca,
DF-UFSC, Florianópolis, CEP 88040-900, SC, Brazil

J.C. Krause,
DCET-URI, Santo Ângelo, CEP 98802-470, RS, Brazil

J.D. Ardisson,
CDTN, Belo Horizonte, CEP 30123-970, MG, Brazil

and M.I. Yoshida
DQ-ICEX-UFMG, Belo Horizonte, CEP 31270-901, MG, Brazil

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$Co_{2+x+y}Mn_{1-x}Al_{1-y}$ intermetallic compounds have been prepared by arc melting and studied with X-ray diffraction and magnetization measurements to ascertain the effect of deviations of composition from the stoichiometry on the ferromagnetism of this system. Hysteresis loops registered at room temperature show a soft ferromagnetic behavior in excess Co. In off-stoichiometric alloys the saturation magnetization is lower than in Co_2MnAl, whereas the Curie temperature T_C is higher in all the studied alloys. T_C varies substantially with variations in composition and increases with the Mn content. In the source of this behavior a volume effect is inferred which is expected to lead to strengthened ferromagnetic exchanges.

Keywords: Heusler alloys; Cobalt; Manganese; Aluminum; Half-ferromagnetic materials

I. INTRODUCTION

The Heusler alloys[1] are of great current interest because of their theoretically predicted half metallicity[2–4]. Theoretical studies of the microscopic origin of the magnetic anisotropy energy in some Heusler alloys indicated that the magnetic coupling has an orbital character and is mainly between atoms of the same species. Experimental findings have also shown that the magnetic properties of these ordered compounds depend significantly upon degree and type of chemical order[5–8]. The stoichiometric Heusler compound X_2YZ crystallizes in the $L2_1$ structure (s.g. Fm3m), which consists of four interpenetrating fcc sublattices, each one occupied by one sort of atom. The Co-based compounds particularly possess higher Curie temperature than the other potential half-metallic compounds, and in some cases, a large decrease of the resistivity with the increase of the temperature has been observed as well as a moderately enhanced specific-heat coefficient and a clear Fermi edge.

A study of the phase stability and magnetic properties of $Co_2Cr_{1-x}Fe_xAl$ has shown that the occurrence of two-phase separation is unavoidable for $x < 0.4$, thus leading to a deviation of the saturation magnetic moments from the Slater-Pauling curve[7]. Moreover, it has been reported that the $L2_1$ phase becomes stable only for $x > 0.7$, where no half-metallic behavior is present. In the earlier studies on the Heusler Co_2MnAl alloy in order to stabilize the $L2_1$ structure was used an annealing of 72 h at 1073 K with a subsequent quenching in water[9, 10]. Reported lattice parameters of the ordered $L2_1$ phase are a = 5.754Å[13] and a = 5.749Å[9]; the Curie temperature is 693 K[9]. From electronic structure calculations magnetic moments of $0.745\mu_B$ and $2.599\mu_B$ have been obtained for Co and Mn atoms, respectively[4]. In the present investigation we examine the effect of variations in the Mn concentration on the structural and magnetic properties of $Co_{2+x+y}Mn_{1-x}Al_{1-y}$ alloys. Since the Mn atoms are carrying the largest magnetic moment in this phase, the intrinsic magnetic properties are expected to be drastically affected as the Mn content is varied. Results of measurements with the experimental techniques of X-ray diffraction, calorimetry and magnetization are discussed in this context.

II. EXPERIMENT

Polycrystalline $Co_{2+x+y}Mn_{1-x}Al_{1-y}$ alloys were prepared by weighing out the required amounts of the constituent materials and arc melting under argon atmosphere in a water-cooled copper crucible. Ingots were then vacuum sealed in quartz tubes and annealed for 3 days at 1273 K, then for more 3 days at 673 K, followed by cooling in the furnace itself. The compositions of the alloys were determined by energy dispersive X-ray analysis (EDX). Room temperature structural analysis was carried out with conventional X-ray diffractometry using Cu-Kα radiation. The magnetic field dependence of the magnetization (M(H)) was registered at room temperature (300 K) in fields up to 850 kA/m. For the calorimetric measurements (TGA) the samples were encapsulated in evacuated quartz glass to avoid oxidation on heating above room temperature up to about 1000 K.

III. RESULTS AND DISCUSSION

For a large variety of Heusler alloys the fully ordered $L2_1$ structure is obtained after a long term annealing in the dis-

TABLE I: Composition, structure, lattice parameters, Curie temperature and unit cell volume of $Co_{2+x+y}Mn_{1-x}Al_{1-y}$ alloys.

composition	structure	a (Å)	c (Å)	V_o(Å^3)	T_C (K)
$Co_{2.31}Mn_{0.48}Al_{1.21}$	$L2_1$	5.744		189.51	706
$Co_{0.78}Mn_{0.13}Al_{0.88}$	fct	3.520	2.855	35.37	787
$Co_{2.29}Mn_{0.57}Al_{1.14}$	$L2_1$	5.738		188.92	740
$Co_{0.76}Mn_{0.16}Al_{0.73}$	fct	3.540	2.825	35.40	778
$Co_{2.30}Mn_{0.60}Al_{1.10}$	$L2_1$	5.744		189.51	740
$Co_{0.76}Mn_{0.17}Al_{0.78}$	fct	3.516	2.846	35.18	770

ordered B2 phase below about 650 K, where the diffusion kinetics are expected to be slow. In some cases a quenching procedure was used to stabilize the B2 phase, whereas in other cases an appropriate annealing followed by furnace cooling (without quenching) was adopted to retain the $L2_1$ phase from the B2 phase, as for instance, to obtain the Fe_2VAl alloy[11, 12]. The X-ray diffraction patterns of the studied alloys are shown in Fig. 1. A profile analysis of the diffractograms with the Rietveld technique indicates the presence of two phases in these samples: the ordered $L2_1$ structure (as the main phase), and a minority phase with a fct structure (s.g. P4/mmm). Some Bragg reflections may be absent due to texturation of the polycrystalline sample. The determined lattice parameters are listed in Table 1, where the indicated compositions are those obtained from the EDX analysis. As it can be seen, close values are observed for the lattice parameters of the ordered $L2_1$ phase in all the studied alloys, in spite of the smaller atomic radius of the Co atom as compared to those of both Al and Mn atoms. For Co_2MnAl, reported values yield a = 5.754 Å[10] and 5.749Å[9]. With the decrease of the Mn concentration down to about half of the stoichiometry the observed variation of the lattice parameter is < 0.3 %. However, the unit cell volume of these alloys is larger than that of Co_2MnAl. In the fct phase, which is tetragonally compressed along the c direction, the cell volume is practically constant and composition independent, despite the variations of a and c.

In Fig. 2 are shown micrographs of the samples taken with EDX. ¿From these it can be seen clearly that these alloys are indeed composed of two phases, which corroborates the results of the X-ray studies. The black spots are voids caused by the etching during surface preparation. From Fig. 2a the formation of two well distinct phases in the $Co_{2.31}Mn_{0.48}Al_{1.21}$ alloy can be easily identified: the gray region corresponds to the main phase with the $L2_1$ structure, while the white region is associated to the minority fct phase. In the spite of the differences in scale, from top to bottom in Fig. 2 one can see how the secondary phase develops and becomes more homogeneously distributed with the increase of the Mn concentration: the white strips tend to proliferate and are becoming shorter in length and more disconnected. One may infer that the morphologies of the two phases appear to be quite different from each other.

The ferromagnetic Curie temperature T_C of the studied alloys was obtained with a magnetobalance. The registered traces are shown in Fig. 3. The measuring field was applied

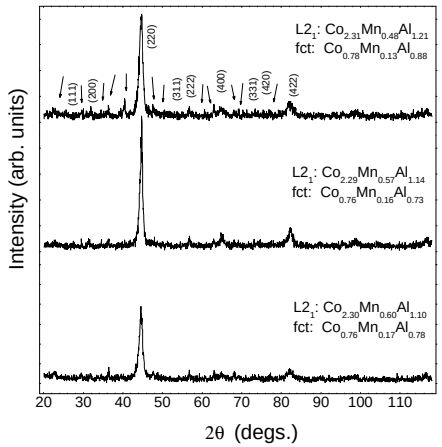

FIG. 1: XRD patterns of $Co_{2+x+y}Mn_{1-x}Al_{1-y}$ alloys; the Bragg reflections of the main phase ($L2_1$) are displayed for the $Co_{2.31}Mn_{0.48}Al_{1.21}$ alloy (top); the arrows indicate peaks of the fct phase.

by means of pieces with H $\lesssim \approx$ 0.5 T. The corresponding T_C values are collected in Table 1. For the $Co_{2.31}Mn_{0.48}Al_{1.21}$ alloy, which has the higher Co content, T_C = 706 K. This result is higher than the previously reported T_C of the stoichiometric alloy (693 K)[13]. As it can be seen in Table 1, with the increase of the Mn concentration the Curie temperature of the $L2_1$ phase is sturdily affected. The unfilled d shells of the Co atoms overlap with those of their Mn neighbors, and so direct exchange thereby becomes possible, and the additional d-electrons of Co atoms causes the strengthening of the ferromagnetic exchanges (Co and Mn spin moments are parallel) which increases as the cell volume decreases and inevitably leads to higher T_C values. Thus, in the source of the observed increase of T_C as compared to Co_2MnAl is a volume effect. As the excess Co atoms in these alloys occupy the Mn sites, stronger interactions are taking place as a result of the increase of the overlap of the d-orbitals, which in turns increases T_C . On the other hand, note that T_C decreases monotonically with the increase of the Mn concentration in the fct phase. The somewhat high T_C values observed for this phase indicates that large spin moments can also be expected for both Co and Mn atoms. In table 1 it can be also seen that, in both phases, at higher Al contents lower T_C values are observed, as one should expect by considering that the Al atoms carry a null

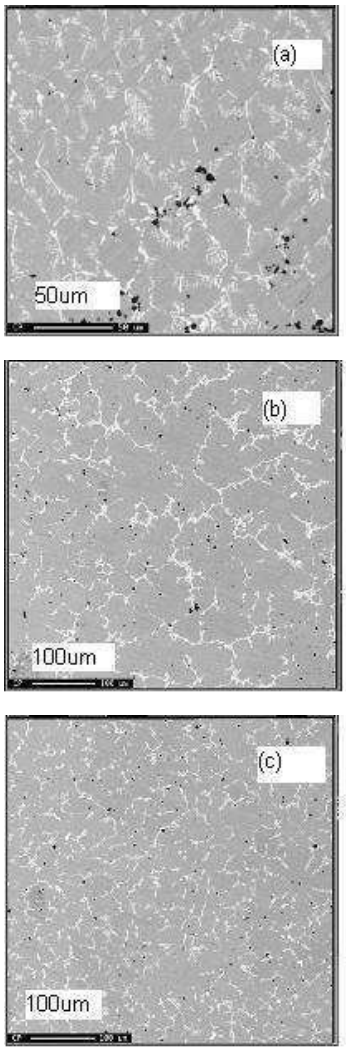

FIG. 2: Micrographs from EDX analysis: (a) $Co_{2.31}Mn_{0.48}Al_{1.21}$ and $Co_{0.78}Mn_{0.13}Al_{0.88}$; (b) $Co_{2.29}Mn_{0.57}Al_{1.14}$ and $Co_{0.76}Mn_{0.16}Al_{0.73}$, (c) $Co_{2.30}Mn_{0.60}Al_{1.10}$ and $Co_{0.76}Mn_{0.17}Al_{0.78}$alloys.

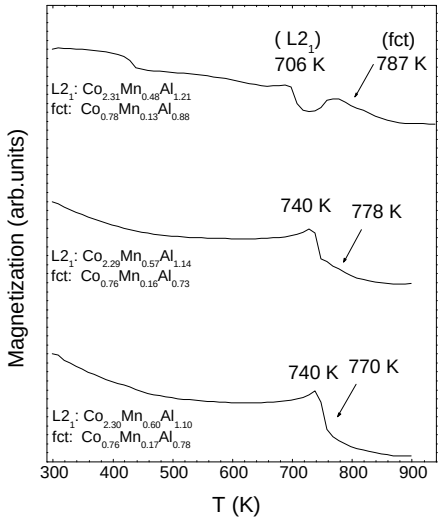

FIG. 3: Transitions measured with a magnetobalance. The Curie temperatures are indicated; the arrows are indicating the transitions associated to the fct phase.

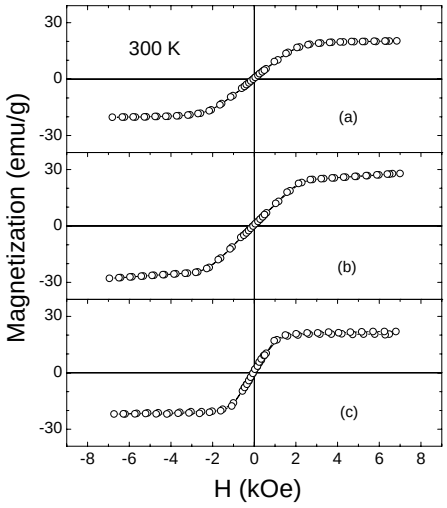

FIG. 4: Hysteresis loops at room temperature of the studied alloys: (a) $Co_{2.31}Mn_{0.48}Al_{1.21}$ and $Co_{0.78}Mn_{0.13}Al_{0.88}$; (b) $Co_{2.29}Mn_{0.57}Al_{1.14}$ and $Co_{0.76}Mn_{0.16}Al_{0.73}$, (c) $Co_{2.30}Mn_{0.60}Al_{1.10}$ and $Co_{0.76}Mn_{0.17}Al_{0.78}$.

moment. Furthermore, the fct phase in the $Co_{0.76}Mn_{0.16}Al_{0.73}$ alloy has a lower T_C as compared to the $Co_{0.78}Mn_{0.13}Al_{0.88}$ alloy, thus indicating weaker ferromagnetic exchanges at this composition in this phase. This feature might be associated to the shrink of the lattice along the *c* direction at this composition.

The hysteresis M(H) loops recorded at room temperature are shown in Fig. 4, which reveal the soft ferromagnetic character of these alloys. Neither remanence nor coercive field are observed. Nevertheless, saturation is attained in applied fields up to about 7 kOe for the $Co_{2.31}Mn_{0.48}Al_{1.21}$ and $Co_{2.30}Mn_{0.60}Al_{1.10}$ alloys. In the $Co_{2.29}Mn_{0.57}Al_{1.14}$ alloy, one sees in Fig. 4 that higher fields are necessary to reach the saturation magnetization, which is higher at this composition. Since any paramagnetic or antiferromagnetic contribution can be ruled out in this case this feature is then associated to the $L2_1$ phase, by considering that the relative amount of the ordered phase is overwhelming in this alloy, as indicated from the X-ray analysis. The reported saturation magnetization M_s at 300 K of Co_2MnAl is 104 emu/g[9]. The obtained M_s results of the $Co_{2+x+y}Mn_{1-x}Al_{1-y}$ alloys are below this value, which indicates that, as Co replaces for Mn, the average magnetic moment decreases steadily, as a consequence of the fact that the Co atoms have smaller moments. It is noteworthy that, according to results of first-principles calculations, as Cr is substituted for Mn in the fully ordered Co_2MnAl al-

loy, the Co spin moment is not affected and so does its orbital moment[4]. The Co moment was found to be mostly induced by the spin-orbit coupling and is insensitive to hybridization with the neighboring sites.

Nevertheless, in the present study the observed behavior of both T_C and M_s can not be explained if one considers that both Co and Mn atoms keep constant moments despite the variations in composition. With the increase of the Mn concentration from $Co_{2.31}Mn_{0.48}Al_{1.21}$ to $Co_{2.29}Mn_{0.57}Al_{1.14}$, T_C and M_s of the $L2_1$ phase increases as a result of the larger moments carried by Mn atoms. Besides, the unit cell volume decreases. Further, from $Co_{2.29}Mn_{0.57}Al_{1.14}$ to $Co_{2.30}Mn_{0.60}Al_{1.10}$ the Al concentration decreases and the Mn concentration increases. However, T_C is unaffected by these changes although M_s decreases. In the framework of constant magnetic moments for both Co and Mn atoms, by considering that the Mn atoms are carrying the largest moments, there would be no reason for the observed decrease of M_s. No contribution from the fct phase is expected therein, since for these alloys the significative change in composition for this phase is in the Al concentration, which increases. Actually the observed trend is indicative that the atomic moments in these alloys are ruled by a subtle mechanism which is strongly affected by changes in composition.

As a conclusion, the results above indicate that with deviations of composition from the stoichiometry, with excess Co, the ordered $L2_1$ structure still can be stabilized in the $Co_{2+x+y}Mn_{1-x}Al_{1-y}$ alloys. However, traces of a secondary phase are observed, which has a fct structure. A remarkable result is the high T_C observed in these alloys for both $L2_1$ and fct phases. In the $L2_1$ phase, T_C is even higher as compared with Co_2MnAl in all the studied alloys. The saturation magnetization at 300 K is higher in the alloy where the unit cell volume is the smallest one. Comparatively, with the variations in the composition of the $L2_1$ phase from $Co_{2.31}Mn_{0.48}Al_{1.21}$ to $Co_{2.29}Mn_{0.57}Al_{1.14}$ the Curie temperature increases from 706 K to 740 K, whereas the saturation magnetization increases and the cell volume decreases. Hence, with the increase of the Co concentration from the stoichiometry one might expect that the Co atoms occupy the Mn sites in the ordered $L2_1$ phase. Thereby the magnetization decreases as a consequence of the smaller Co moments, although a strengthening of the ferromagnetic exchanges takes place, as indicated by the increased T_C values of these alloys.

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