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Electric and Magnetic Signatures of Structural and Chemical Ordering of Heusler Alloy Films

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We present results of *in situ* temperature measurements of resistivity for some amorphous or partially crystalline Heusler alloy films: Co_2CrAl, Co_2MnGa and off-stoichiometric $Ni_2Mn_{1+x}Sn_x$, $Ni_2Mn_{1-x}Ga_x$ that are known to exhibit half-metallic properties and martensitic transformations, respectively. From ρ vs. T characteristics we distinguish various stages of chemical and structural ordering in the films. They appear to be quite distinct in both systems investigated. The resistivity results are compared with magnetic characteristics for Co_2MnGa with a high Curie temperature.

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1. Introduction

Thin films of Heusler alloys (HA) are important for applications in spintronics or in devices based on shape memory effect (for review papers, see for example Refs. [1, 2]). Epitaxial HA films prepared by molecular-beam epitaxy have been shown to grow pseudomorphically on GaAs substrates with $L2_1$ or $B2$ structures [3]. Frequently, however, HA films have been deposited by sputtering [4, 5], laser ablation [6], or flash-evaporation [7] at room temperature (RT) with subsequent annealing. HA films deposited at RT or lower temperatures have, as a rule, highly disordered structure (amorphous or partially crystalline) [7] and chemical disorder significantly different from that of typical HA with $L2_1$ or $B2$ structure. In bulk HA ordering is typically achieved by annealing at temperatures as high as 1000–1300 K for many days, but in HA films such a procedure is obviously unacceptable. In this contribution we present the results of *in situ* resistivity measurements of several disordered HA films. We show how the ordering in HA films can be monitored with the resistivity measurements. Under proper annealing conditions, properties typical of bulk ordered HA counterparts can be almost fully restored. The results of resistivity measurements are compared with the magnetic characteristics of Co_2MnGa films.

2. Experimental and results

Films of Co_2CrAl, Co_2MnGa and off-stoichiometric $Ni_2Mn_{1+x}Sn_{1-x}$ ($x = 0.4$) were prepared by flash evaporation [7] from HA powders of proper composition onto liquid nitrogen cooled glass substrates. The off-stoichiometric $Ni_2Mn_{1+x}Ga_{1-x}$ ($x = 0.15, 0.4$) films were prepared by rf-sputtering at room temperature. The Ni–Mn–Ga and Ni–Mn–Sn films with off-stoichiometric composition were chosen since they reveal the martensitic transformation at higher temperatures than that of stoichiometric compounds [2]. Film thicknesses were between 100–200 nm except the sputtered Ni–Mn–Ga film with thickness of 2 μm and were measured with Dectak profiler or by X-ray fluorescence (XRF). Film composition was determined with XRF. Structure of the films was determined with X-ray diffraction (XRD) using Cu K_α or Co K_α radiation. The films were amorphous or partially crystalline except the Ni–Mn–Ga sputtered films in which XRD shows a single broad (220) peak typical of microcrystalline $A2$ structure of fully disordered HA structure. In as-deposited state the films were nonmagnetic or very weakly magnetic (Co_2MnGa) and after ordering they revealed crystalline $B2$ or $L2_1$ [7, 8] or tetragonal [2] structure and show ferromagnetic ordering. The resistivity measurements were carried *in situ* in a high-vacuum chamber used for flash-evaporation at temperature varying from 300 to 800 K with a scan rate of 4 K/min. For Ni–Mn–Ga and Ni–Mn–Sn films with shape memory effect the resistivity measurements were also carried out from 200 to 400 K in a low-temperature setup. Magnetic measurements were performed using ferromagnetic resonance (FMR) spectrometer at 9.08 GHz and vibrating sample

magnetometer (VSM) at a temperature range from about 200 K up to 600 K.

Figure 1 shows changes in the resistivity of Ni–Mn–Ga, Ni–Mn–Sn, Co_2CrAl and Co_2MnGa films during temperature cycling from 300 to 700–800 K and back to 300 K. After high temperature cycling, we also performed additional $\rho(T)$ measurements in a temperature of 200 to 400 K. Usually, upon crystallization of amorphous alloys, the resistivity decreases about twice [9] due to increase in structural and chemical ordering. In disordered Ni–Mn–Ga(Sn) films, we observe a similar effect, however less noticeable: the resistivity decreases by 60–70%. Comparing Fig. 1a with b, one can notice that disordered Ni–Mn–Ga films are more resistant to ordering than Ni–Mn–Sn films, for which the resistivity decreases abruptly at about 520 K due to crystallization. This is in accordance with results of extended X-ray absorption fine structure (EXAFS) [10] measurements, which proved that the successive appearance of ferromagnetic and shape memory properties in annealed Ni–Mn–Ga films are related to the change in chemical ordering and then to an increase in crystalline grain structure, respectively. In the case of our Ni–Mn–Ga(Sn) films, the ferromagnetic ordering was achieved after full thermal cycle since in both films the characteristic "kinks" on $\rho(T)$ are clearly seen at the Curie temperature $T_C \approx 380$ K and $T_C \approx 320$ K, respectively (see Fig. 1a and b). Inset in Fig. 1a shows $\rho(T)$ for a $Ni_{1.92}Mn_{1.48}Ga_{0.6}$ film. The main features of $\rho(T)$ upon crystallization are similar to that of $Ni_{1.94}Mn_{1.21}Ga_{0.85}$ film but after ordering at ≈ 800 K a hysteretic anomalous jump in ρ is seen at temperature range of 300–400 K. This is typical of martensitic transformation in Ni–Mn–Ga films with shape memory effect [11].

In Figs. 1c and d it is seen that for Co_2CrAl and Co_2MnGa films $\rho(T)$ characteristics are significantly different from that of Ni–Mn–Ga(Sn) films. The resistivity of amorphous Co_2CrAl film abruptly increases at $T \approx 500$ K and after ordering it attains higher values. Moreover, after ordering at 600–700 K the temperature coefficient of resistivity TCR > 0 in accordance with earlier observations [12] for $L2_1$ ordered bulk Co_2CrAl. On crystallization and ordering of the amorphous Co_2MnGa film the resistivity also increases, however in a different way. Figure 1d shows clearly that at ≈ 430 K, the electrical resistivity experiences a substantial jump-like increase and then at ≈ 500 K, it decreases in a similar way but attains values by about 30% higher than those in the amorphous state. With independent XRD and transmission electron microscopy (TEM) measurements [8] we checked that low-temperature annealing at ≈ 500 K leads to a very inhomogeneous mixed phase consisting of Co_2MnGa and ϵ-Mn_3Ga (and/or Mn_3Co_7) phases.

Annealing of our HA films can restore single phase ordered HA structures, which are ferromagnets with the Curie temperatures typical of bulk alloys. Due to limited space, we would like to discuss more thoroughly characteristic changes in magnetic properties during the crystallization process of the amorphous Co_2MnGa films and to compare them with the resistivity data shown in Fig. 1d. Since the Curie temperature of the ordered Co_2MnGa is of 690 K, it is possible to monitor *in situ* the changes in the magnetic characteristics of the disordered film in the course of heating and cooling back to RT. Figures 2a and b show the temperature dependence of the effective magnetization $4\pi M_{\text{eff}}$ and saturation magnetization M_S, respectively. $4\pi M_{\text{eff}}$ and M_S were derived from FMR and VSM measurements, respectively. The amorphous Co_2MnGa is already very weakly magnetic: there is seen a weak FMR signal though it has practically no magnetic moment measured with VSM. It is seen that $4\pi M_{\text{eff}}$ also experiences substantial changes in the same temperature range as the resistivity (Fig. 1d). As shown in Fig. 2b, the saturation magnetization M_S does not change until about 500 K and then begins to increase to a value of 250 G in a range of 500–600 K. It is reasonable to conclude that crystallization of the amorphous Co_2MnGa films, occurring below ≈ 520 K, leads to a strongly inhomogeneous polycrystalline structure in accordance with the resistivity measurements. Further ordering leads to an enhancement of the magnetic characteristics of the Co_2MnGa films: the RT values of $4\pi M_{\text{eff}}$ increase up to 6000 G and M_S to ≈ 500 G. To conclude, our resistivity and magnetic measurements of the amorphous Co_2MnGa films at elevated temperatures show clearly nonmonotonic changes resulting from appearance of mixed phases at 520 K followed by further homogenization and ordering at $T \approx 600$ K.

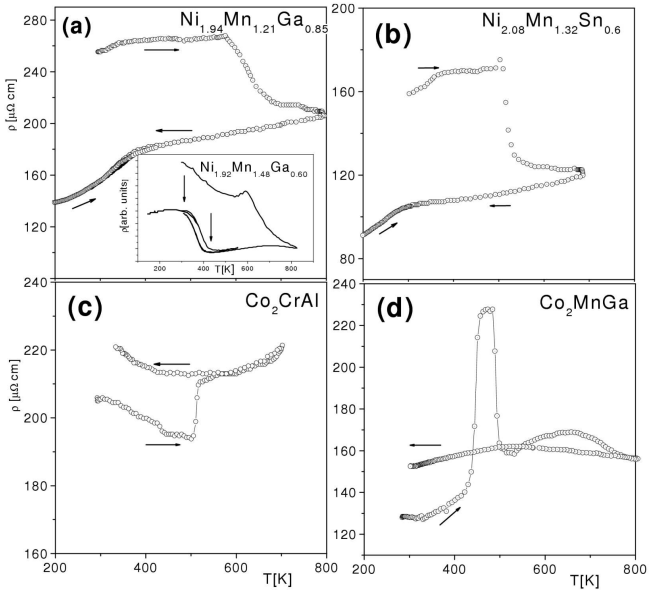

Fig. 1. Exemplary temperature changes in resistivity ρ for the disordered Ni–Mn–Ga (a), Ni–Mn–Sn (b), Co_2CrAl (c), Co_2MnGa (d) on high temperature cycling. Inset in (a) shows $\rho(T)$ characteristic with a hysteretic behavior between 300 and 420 K typical of ordered off-stoichiometric Ni–Mn–Ga alloys.

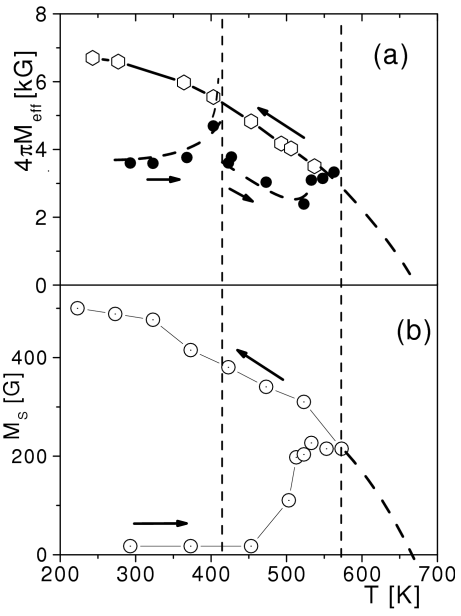

Fig. 2. (a) Changes of the effective magnetization $4\pi M_{\text{eff}}$ and (b) in the saturation magnetization M_{S} of an amorphous Co_2MnGa film in the course of heating and cooling back to RT.

3. Conclusions

We investigated high temperature resistivity in amorphous Co_2MnGa, Co_2CrAl and partially crystalline off-stoichiometric Ni–Mn–Ga, Ni–Mn–Sn films. Structural disorder severely affects the conduction electron mean free path as well as the exchange interactions resulting in the high resistivity and the lack of ferromagnetic ordering. Generally, at temperatures of ≈ 500 K (Co_2MnGa, Co_2CrAl) or ≈ 600 K (Ni–Mn–Ga, Ni–Mn–Sn) the films crystallize. However, our results show that chemical and structural ordering may have diverse effect on high temperature characteristics of HA films. Resistivity may decrease almost monotonically over a wide temperature range from 600 to 700 K (Ni–Mn–Ga). It may drop (Ni–Mn–Sn) or rise (Co_2CrAl) in a narrow temperature range or it may show a characteristic maximum (Co_2MnGa) due to appearance of mixed phases, which were confirmed with the magnetic measurements. In conclusion, high temperature resistivity measurement is a sensitive tool for tracing the chemical and structural ordering in HA films.

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