# INFLUENCE OF STRUCTURAL ORDER
# ON MAGNETIC PROPERTIES
# OF Ni₂MnIn HEUSLER ALLOY FILMS

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**Abstract:** We report structure and magnetic properties of polycrystalline and amorphous Ni₂MnIn films deposited by flash-evaporation onto glass, Si, mica substrates at 150, 545, 660 and 730 K. Depending on the substrate temperature $T_s$, the films show in X-ray diffraction the presence of the ordered L2₁ crystal structure ($T_s$ = 730 K), a B2 structure ($T_s \approx$ 545-660 K) or are amorphous-like ($T_s$ = 150 K). Magnetic properties of our polycrystalline films correlate with their structural order. The highest saturation magnetization ($M_S$ = 400 G) and effective magnetization ($4\pi M_{eff} \approx$ 3000 G), $T_C$ = 320 K, and a low ferromagnetic resonance linewidth ($\Delta H \approx$ 200 Oe at room temperature) are observed for the films with ordered L2₁ structure while the films with lower structural ordering (B2) have a substantially lower magnetization and a very large linewidth of 1000-2000 Oe due to an inhomogeneous broadening. The amorphous films have no ferromagnetic order. Annealing of amorphous films at temperatures of 630-640 K results in growth in the structural order and leads to ferromagnetic ordering with nearly the same magnetization and the Curie temperature as the films with L2₁ structure.

## 1. INTRODUCTION

Ni₂MnIn Heusler alloy is regarded as a promising candidate for spintronic applications since, according to the band structure calculations [1], it shows an energy gap between the valence and conduction bands for the minority electrons and a continuous band for the majority electrons. Recent experimental attempts [2, 3] aimed at producing by the molecular beam epitaxy (MBE) single crystalline Ni₂MnIn films on a InAs semiconducting substrate showed, however, a substantial departure of their basic magnetic properties from those of bulk Ni₂MnIn. It has been shown that epitaxial growth of Ni₂MnIn on InAs(001) results in the B2 crystal structure of the films with a low Curie temperature of about 170 K [2] or a disordered L21 structure (a CsCl structure) with a Curie temperature of about 290 K [3]. In bulk, Ni₂MnIn is reported to have a cubic (L21) crystal structure with lattice constant $a$ = 0.607 nm and a Curie temperature $T_C$ of about 314 K [4]. On the other hand, the polycrystalline films deposited by co-evaporation on InAs or Si substrates at elevated temperatures show the expected cubic structure L2₁ and reveal ferromagnetic ordering at room temperature [5].

The present contribution reports structure and magnetic properties of polycrystalline and amorphous Ni₂MnIn films deposited by flash-evaporation onto glass, Si and mica substrates. Depending on the substrate temperature $T_s$, the films reveal various types of structural ordering. The magnetic properties of the flash-evaporated Ni₂MnIn are shown to be correlated with their structural ordering.

## 2. EXPERIMENTAL

The 100-200 nm thick $Ni_2MnGa$ films were deposited by flash-evaporation in a vacuum better than $5 \times 10^5$ Pa of the alloy powders onto glass, Si or mica substrates kept at 150, 545, and 730 K, respectively. For evaporation we used the powders obtained from a carefully prepared $Ni_{0.502}Mn_{0.248}In_{0.250}$ ingot. The flash-evaporation method results in film composition identical to that of the source material [6]. Several thin film samples were made using different substrate temperatures. Here, we present the results for $Ni_2MnIn$ deposited on glass substrates at three different substrate temperatures: 730 K (sample A), 545 K (sample B) and 150 K (sample C). Sample C was additionally annealed at 640 K for 30 min. This sample will be referred to as sample C ann. These samples are the most representative for the whole set of the flash-evaporated $Ni_2MnIn$ films. Additionally for the samples deposited at 545 K the effect of substrates will be also shortly discussed. The structural characterization of the films was carried out by X-ray diffraction (XRD) using Cu $K_\alpha$ radiation. The XRD study included grazing incidence and out-of-plane Bragg $\Theta$–$2\Theta$ scans. Magnetic properties of the films were measured using a superconducting quantum interference device magnetometer (SQUID) from 4 to 350 K and using a standard homodyne ferromagnetic resonance (FMR) spectrometer operating at $f$ = 9.08 GHz in a temperature range from 78 to 450 K.

## 3. RESULTS

Figure 1 shows the XRD scans of samples A, B, and C ann. The scans were taken in the grazing incidence geometry to detect more diffraction peaks (for details see Ref. [7]). The XRD of sample C deposited at 150 K reveals only a broad maximum centered at $2\Theta$ of about $40^\circ$ which is typical result of the amorphous Heusler alloy films [8]. Film A deposited at 730 K on glass shows in XRD the presence of the (111) Bragg reflection typical for the Heusler alloys with $L2_1$ structure, since in polycrystalline Heusler alloys the relative intensity of the superstructure Bragg reflection (111) is conveniently used to determine the degree of disorder introduced by Mn $\leftrightarrow$ In exchange [4]. Moreover, the presence of other reflection implies a polycrystalline, non-textured microstructure of the film. This is in a strong contrast to pseudomorphic $Ni_2MnIn$ films grown on InAs substrates by using MBE, where only (001) and (002) reflections were observed [2]. The (220) and (422) reflections are split due to some tetragonal distortions of the crystal lattice. We estimate the tetragonal distortion to be about $a/c$ = 0.987 with $a$ = 0.614 nm. This lattice constant is in agreement with the values reported by Xie *et al*. [2] (0.613 nm) or Dong *et al*. [3] (0.615 nm) and higher than a value of 0.6024 nm estimated by Kurfis *et al*. [5]. The presence of small tetragonal distortion is not clear since $Ni_2MnIn$ is known to have no martensitic transformation typical of $Ni_2MnGa$ [4] – the most interesting Heusler alloy exhibiting a ferromagnetic shape-memory effect. The XRD pattern of sample B deposited at 545 K shows no (111) reflections and the presence of a strong (200) reflections implies that a B2 structural order [2] is established for these deposition conditions. The amorphous $Ni_2MnIn$ film after annealing (sample C ann.) shows nearly the same XRD pattern as sample A (Fig. 1) what suggests that the structural ordering can be established by a proper annealing of an amorphous film of $Ni_2MnIn$.

Fig. 1. X-ray diffraction patterns from sample A (Ni$_2$MnIn film deposited at 730 K) and sample B (Ni$_2$MnIn film deposited at 545 K) and annealed sample C (Ni$_2$MnIn amorphous film annealed at 640 K for 0.5 hr). The X-ray diffraction were taken at grazing incidence angle of 2° with Cu $K_\alpha$ radiation
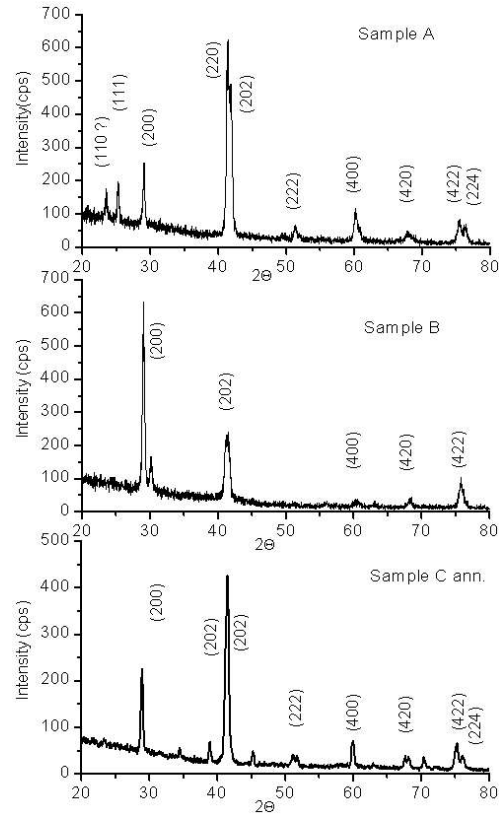
Figure 2 shows the temperature dependences of magnetization of the samples A, B and C. The magnetization was measured with an in-plane magnetic field of 1 T. The saturation magnetization of sample A extrapolated to 0 K is nearly 400 G, nearly the same as that reported for bulk ordered Ni$_2$MnIn [4], while the saturation magnetization of sample B is two times smaller. However, the estimated error in absolute magnetization values is high (about 50 G) since diamagnetic moment of the glass substrates is comparable with the magnetic moment of the films and a low temperature part of magnetization dependence is additionally obscured by a high paramagnetic component due to the presence of ions in glass. Nevertheless, in agreement with other data [2, 3], the magnetization in thin Ni$_2$MnIn Heusler alloy films may vary in a wide range depending on deposition conditions and structural order. It is a very well known fact that the magnetic properties of Heusler alloys are sensitive to ordering and chemical composition [4]. The Curie temperature estimated on the basis of our magnetization dependences (Fig. 2) is substantially higher than 314 K reported in literature [4, 5] since a large magnetic field of 1 T was applied. Our low-field (0.01 T) magnetization measurements (not shown here) give a more convincing value of 320 K. Additionally, we have checked that the amorphous film (sample C) shows no ferromagnetic ordering in a temperature range from 4 to 350 K (Fig. 2). This result is in agreement with our earlier studies on the influence of the structural ordering on magnetic properties of Ni$_2$MnGa films [8]. In accordance with our

structural data (Fig. 1), after annealing of the amorphous Ni$_2$MnIn film, the magnetization typical of well ordered films can be almost fully recovered (see two data points in Fig. 2 for sample C ann.).
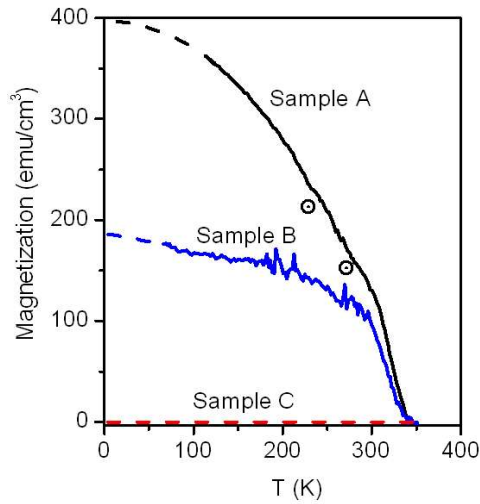


Fig. 2 Temperature dependence of magnetization of Ni$_2$MnIn films deposited at 730 K (sample A), 545 K (sample B), and 150 K (sample C). Two data points (circles) show the magnetization of sample C after annealing at 670 K for 0.5 hr
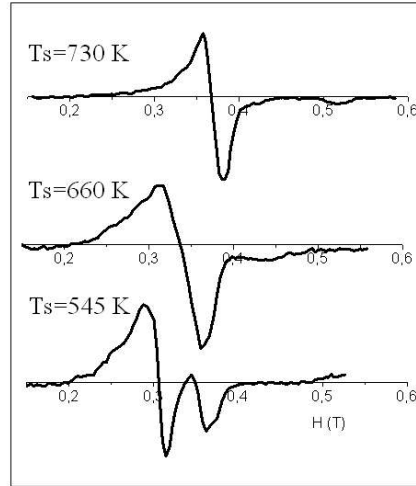
Fig. 3 FMR spectra of Ni$_2$MnIn films deposited on glass substrates at 545, 660, and 730 K

Our structural investigations and magnetization measurements have shown that the films deposited at temperatures lower than 730 K are structurally and magnetically inhomogeneous. FMR is one of the best method for probing the magnetic quality of thin films [9]. In particular, narrow FMR lines are typical of the films with a high degree of magnetic homogeneity [10]. As shown in Fig. 3, the linewidth for the more ordered films (*e.g.* sample A) is as low as 200 Oe but it increases strongly to about 600 Oe for the samples deposited at lower temperatures and also depends on the substrates. It is seen in Fig. 4 that the films deposited on glass and Si (oxidized) substrates give nearly the same FMR responses while that deposited on mica substrate shows substantially broader FMR spectrum which is located at higher fields. For some samples deposited at $T_S$ < 730 K, the linewidth is as high as 1000-2000 Oe. This simply shows that fabrication of a good (*i.e.*, well ordered) Heusler alloy thin film sample is not a trivial problem. Usually, even in the case of the well ordered films, the FMR spectra consist of 2-3 lines (see Fig. 3). Figures 5 (a)-(c) show for each line the temperature dependencies of the resonance fields taken with a magnetic field applied perpendicular to the film plane (the so-called perpendicular configuration). It is seen (Fig. 5 (a)) that the trend in the temperature dependence of the saturation magnetization $4\pi M_S(T)$ is qualitatively followed by
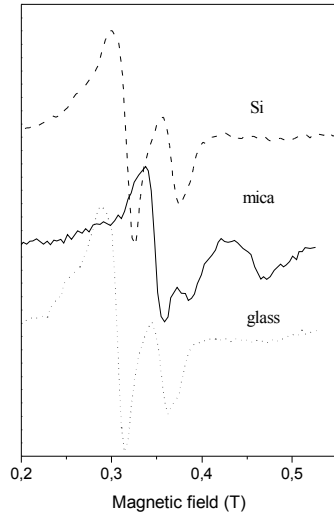
Fig. 4. FMR spectra of Ni$_2$MnIn films deposited at 545 K on Si, mica and glass substrates. The spectra were taken with a magnetic field applied perpendicular to the film plane
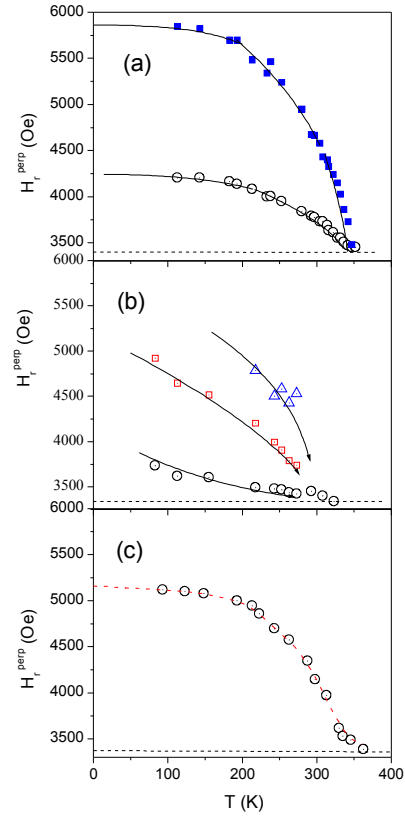


Fig. 5. Temperature dependencies of FMR resonance fields taken at the perpendicular configuration for Ni$_2$MnIn films deposited at various temperatures on glass substrates. (a) sample A – deposited at 730 K, (b) sample B – deposited at 545 K, (c) sample C ann. – deposited at 150 K and annealed at 640 K for 30 min.

$H_r(T)$ measured in sample A. This is not the case for sample B (Fig. 5 (b)) where the most intensive line has a concave temperature dependence. On the other hand, an annealed amorphous film (Fig. 5 (c)) shows only a single FMR spectrum which follows the general trend in temperature dependence of the saturation magnetization $4\pi M_S(T)$. Generally, the most characteristic feature of the FMR data is that the resonance fields are much lower than it would be expected from a simple resonance condition for the thin films at the perpendicular configuration: $H_r = 4\pi M_S + \omega/\gamma$ where $\omega$ is the angular microwave frequency $\omega = f/2\pi$ and $\gamma$ is the giromagnetic ratio. Since $\omega/\gamma$ is of about 3.35 kOe for the $g$-factor of 2.1 [7], the resonance field at low temperature should be of about 8.4 kOe ($M_S = 400$ G, see Fig. 2). The highest

resonance field for sample A is of only ~6 kOe what suggests that the effective magnetization $4\pi M_{\text{eff}} = 4\pi M_S\ 2K_u/M$ of sample B is of about 2.4 kOe lower than $4\pi M_S$. This means that a substantial perpendicular anisotropy field $2K_u/M$ of 2.4 kOe should exist in the film. In the films with lower degree of ordering (Figs. 5 (b)-(c)), the perpendicular anisotropy is lower and amounts to about 1 kOe. Due to limited available space we can only qualitatively explain the FMR results. Both large value of perpendicular anisotropy and multipeak structure of the FMR spectra suggest that the perpendicular anisotropy in $Ni_2MnIn$ films is actually a strain-induced anisotropy field created through the phenomenon of magnetostriction. We have no magnetostriction data for $Ni_2MnIn$, but generally in Heusler alloys the magnetostriction is highly anisotropic ($\lambda_{100} \neq \lambda_{111}$) [11] and if the films are subjected to a large planar strain the appropriate calculations based on the independent-grain approach with randomly oriented grains predict characteristic singularities in FMR absorption [12]. Our rough estimation with $\lambda_{100} = 300 \times 10^6$, $\lambda_{111} = 30 \times 10^6$ [11] and a reasonable value of the planar stress of $\sigma = 1 \times 10^9$ $dyn/cm^2$ gives a stress induced anisotropy field of about 2-3 kOe and approximately the same positions of the singularities in FMR absorption that corresponds to the multipeak nature of FMR spectra. The spectra of sample B presented in Fig. 4 may serve as an example that the singularities in FMR absorption are very typical for the $Ni_2MnIn$ films. They also shows that the influence of substrate may be important due to difference in stress and, possibly, a texture.
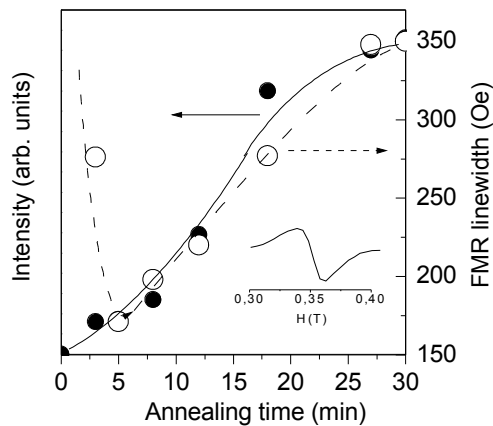


Fig. 6. Effect of annealing of amorphous $Ni_2MnIn$ film (sample C) on the intensity of FMR spectrum (full dots) and its width $\Delta H$ (open dots). The intensity is proportional to the magnetic moment of the film. The inset shows the FMR spectrum of sample C ann. after annealing

The main problem with technology of thin films of Heusler alloys is that independent of deposition method used, the substrate temperature $T_S$ should be high enough to ensure the formation of $L2_1$ structure, which is the most ordered structure [4]. This requirement induces a lot of problems, since at high $T_S$ there is a high degree of interdifusion between a substrate and the film. Therefore, it is more convenient to deposit the Heusler alloy films at lower temperatures with (quasi)-amorphous structure and then anneal them at elevated temperatures to obtain the films with a high degree of structural ordering. We applied such a procedure to the amorphous film deposited at 150 K by annealing it at 640 K for several minutes. In result of the annealing we received the film with a high degree of structural order

as can be seen from Fig. 6, where a FMR intensity (defined as the area under FMR absorption curve) and FMR line width $\Delta H$ are plotted versus the annealing time. This result is also supported by the XRD data. It is seen in Fig. 6 that the intensity (proportional to a magnetic moment of the film) increases with time and tends to saturate in a way typical of thermally activated process. Meanwhile, the linewidth $\Delta H$ attains the minimum and then increases to values typical of the films fabricated at elevated substrate temperatures (see inset in Fig. 6). A feature of technological importance is that mild annealing of amorphous films at 640 K for several minutes produces a fairly well ordered structure.

## 4. SUMMARY

In summary, we have presented structural and thermomagnetic results obtained for a series of Ni$_2$MnIn thin films grown by flash-evaporation at substrate temperatures $T_S$ ranging from 150 to 730 K. The films are single phase and fine-crystalline or amorphous for the lowest $T_S$. The films deposited at the highest substrate temperature of 730 K have L2$_1$ structure with a small tetragonal distortion. As the substrate temperature decreases, the films tend to grow in B2 type of structure and, eventually, those deposited at 150 K are amorphous and non-magnetic. Magnetic properties of the flash-evaporated Ni$_2$MnIn thin films correlate with their structural order and magnetic properties typical of the well ordered bulk Ni$_2$MnIn [4] are attained in films deposited at the highest $T_S$. FMR data analysis suggests that the films are magnetostrictive what results in a substantial perpendicular anisotropy and multipeak structure of the FMR spectra. Annealing of the amorphous films at temperatures of 630-640 K results in the growth in structural order and leads to ferromagnetic ordering.

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