We study the temperature dependence of strain under constant magnetic-fields in Ni-Mn based ferromagnetic Heusler alloys in the form Ni-Mn-X (X: Ga, In, Sn, Sb) which undergo a martensitic transformation. We discuss the influence of the applied magnetic-field on the nucleation of ferromagnetic martensite and extract information on the easy-axis of magnetization in the martensitic state.

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At off-stoichiometric compositions with respect to the 2-1-1 stoichiometry, almost any Ni-Mn based ferromagnetic Heusler alloy in the form Ni-Mn-X (X: group IIIA - VA elements) undergoes a martensitic transformation [1][2][3][4]. Ni$_5$MnGa is the only Ni-Mn-based Heusler that undergoes such a transition in the 2-1-1 stoichiometry [5]. This occurs at roughly 240 K, and it exhibits large magnetic-field-induced strains in the martensitic state. Many of the off-stoichiometric alloys with X as In, Sn, Sb, etc., exhibit a magnetic-field-induced reverse martensitic transformation from the martensitic to the austenitic state and is usually accompanied by large strains [6][7][8] and magnetocaloric effects [9][10][11]. These effects are closely related to the strength of the magnetoelastic coupling in the martensitic state.

A knowledge of the magneto-crystalline anisotropy is particularly important to be able to understand the subtleties associated with the coupling between the magnetic and structural degrees of freedom, this being responsible for large strains and entropy changes around the transition temperature [12][13]. Anisotropy studies usually require single crystals of bulk or thin film specimens on which various experimental techniques such as neutron diffraction, ferromagnetic resonance, magnetic circular dichroism, torque studies, etc. can be performed. These can provide information on the easy-axis of magnetization and on the orbital and spin moments, which are prime parameters for understanding the magnetic anisotropy, and, therefore, the magneto-crystalline anisotropy.

In the L1$_0$ phase, having two $a$-axes and a $c$-axis, or in any modulated martensitic structure, the magnetization will tend to lie either in a plane bounded by the $a$-axes or along the $c$-axis of the unit-cell. We demonstrate in this study that by using polycrystalline specimens, it is possible to provide information on the easy-axis of magnetization in the martensitic structure with temperature-dependent strain measurements under constant magnetic-field. We present results on such measurements for the martensitic Heusler alloys Ni-Mn-Sn, Ni-Mn-In, and Ni-Mn-Sb; as well as Ni-Mn-Ga, which serves as a reference system for which the easy-axis of magnetization in the martensitic state is known to be along the short-axis [5].

Ingots were prepared by arc melting pure metals under argon atmosphere in a water cooled Cu crucible.
They were then encapsulated under argon atmosphere in quartz glass, annealed at 1073 K for 2 hours and, afterwards, quenched in ice-water. The compositions of the alloys were determined by energy dispersive x-ray analysis. Temperature-dependent strain measurements in magnetic-fields up to 5 T were carried out using strain gauges. The field was first applied in the austenitic state, and the data were subsequently taken on decreasing and then on increasing temperature. The strain was measured parallel to the applied field.

The relative length-change $\Delta l/l$ referenced to 300 K and in magnetic-fields up to 5 T for Ni$_{49.6}$Mn$_{27.3}$Ga$_{23.1}$ is shown in Fig. 1(a). In the absence of a magnetic-field, a weak hysteretic feature is found in the temperature range corresponding to that of the martensitic transition, and no substantial difference in the macroscopic dimensions between the austenitic and martensitic states is found. Applying a magnetic-field in the austenitic state has very little influence on the strain in this state. However, when the sample is subsequently cooled through the martensitic transition temperature $M_s$, a large difference in the strain between the austenite and martensite states occurs. This effect has previously been observed in a single-crystal specimen and is due to the alignment of the short easy-axis of magnetization (c-axis) with the external field, causing the sample to shrink along the applied field direction $\hat{c}$. With increasing measuring field, the difference in strain increases due to increased preferred alignment of the short c-axis along the applied field. High twin-boundary mobility in Ni-Mn-Ga is expected to be the main cause of the alignment, although martensite variant nucleation with preferred c-axis orientation in the external field already just at $M_s$ is also an influence on the shrinkage.

Ni$_{49.8}$Mn$_{34.7}$Sn$_{15.5}$ undergoes a martensitic transformation at about 120 K. As seen in Fig. 1(b), cooling in the absence of a magnetic-field leads to a raid drop in $\Delta l/l$ at $M_s$ indicating a volume decrease. The presence of this volume decrease is sustained by temperature-dependent neutron diffraction experiments [14]. Cooling in the presence of a magnetic-field causes $M_s$ (indicated by arrows) to drop at a rate of about $-3\,K/T$. At the same time, the difference in strain between the austenite and martensite states increases with increasing magnetic-field as in the case of the data of the Ni-Mn-Ga sample in Fig. 1(a). However, twin boundary mobility in Ni-Mn-Sn sample is weak, so that only little magnetic-field-induced strain ($\sim 10^{-5}$) is observed in fields up to 5 T after cooling the sample through $M_s$ in zero-field to 110 K (inset Fig. 1(b)). Therefore, the large change in strain ($\sim 10^{-3}$) between the austenite and martensite states in this material should be related to the effect of the magnetic-field in providing a preferred orientation for the martensite variants during their nucleation. Since the strain difference increases with increasing magnetic-field (meaning that the sample-length decreases with increasing cooling-field), the easy-axis of magnetization in the martensitic state is expected to be along a short-axis or at least in a plane bounded by the short-axes.

The situation for Ni$_{50.3}$Mn$_{33.7}$In$_{16.0}$ is the opposite: As seen in Fig. 2(a), the cooling-field acts to decrease the relative length-change between the austenite and the martensite states. This can happen if the long-axis of a martensite variant is preferred along the field direction, which would indicate that a long-axis is the easy-axis of magnetization. The rate of change of $M_s$ with applied field for this sample is about $-10\,K/T$, being about 3 times larger than that for the Ni-Mn-Sn sample.

The data for Ni$_{50.3}$Mn$_{35.9}$Sb$_{13.8}$ is similar to that of Ni$_{50.3}$Mn$_{33.7}$In$_{16.0}$ Fig. 2(a). Here, the rate of decrease of $M_s$ with applied field is about $-1\,K/T$. The relative length-change between the austenite and martensite states in applied field also decreases with increasing applied field but, above 2 T further decrease becomes insignificant. In this case also, the easy-axis is expected to be a long-axis.

For the measurements of all samples presented above, the data are reproducible on cycling through the transition temperatures under zero-field or under the presence of a field. Microscopic morphological modifications such as cracks or other deformations, which could occur during cycling and lead to irreproducibilities in the strain-data, are not found.
FIG. 3: Schematic representation of ferromagnetic martensite nucleation with and without a cooling magnetic-field applied at \( T > M_s \). Twins are represented with tetragonal units of length \( l \) built up of self-similar tetragonal unit-cells. There is no preferred variant growth during martensite nucleation when cooled in \( H = 0 \). Preferred variant growth during martensite nucleation when the sample is cooled through \( M_s \) in \( H > 0 \), such that when the long-axis is the easy-axis, the length increases in field direction by \( \delta \). When the short-axis is the easy-axis the length decreases by \( \delta \) in the field direction.

It is known that when a martensitic material is cooled through \( M_s \) under zero applied field, the martensitic variants self-organize forming twin-related structures in order to minimize the elastic energy associated with the change of shape of the unit-cell. This minimizes the macroscopic deformation due to the structural transformation. The data presented here suggests that when cooling the system through \( M_s \) under an applied magnetic-field, martensite variants can nucleate and grow with a preferred orientation within the austenitic matrix. The particular orientation would depend on the direction of the applied field and the direction of the easy-axis of magnetization in the martensitic phase. In this case, considerable modifications in the macroscopic strain can be obtained with respect to the case where the sample is cooled in the absence of a field. This nucleation mechanism does not depend on the mobility of the martensitic variants.

As a summary, we show schematically in Fig. 3 the effect of a cooling magnetic-field on martensite nucleation probed through strain. In this figure, 90° twins are represented with tetragonal units of length \( l \) built up of self-similar tetragonal unit-cells. When a sample is cooled through \( M_s \) in the absence of a field, no preferred direction is given to variant-growth during nucleation, whether the easy-axis of magnetization is a long-axis or a short-axis. When a field is applied in the austenitic state and the sample is cooled through \( M_s \) in this field, a preferred growth-direction is provided to the variants. Variants with easy-axis along the applied field direction nucleate more. If the easy-axis is the long axis, the sample-length measured along the field direction increases by an amount to \( l + \delta \). If the easy-axis is the short-axis, the sample-length decreases to \( l - \delta \). In this manner, it is possible to gain an idea on the easy-axis of magnetization in the martensitic state using polycrystalline specimens, and further studies on anisotropy properties can be carried out using such results.

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