Experimental report

16/10/2017

Proposal: 5-32-841 **Council:** 10/2016

Title: SANS polarization analysis on Ni-Mn-In shape-memory alloys: existenceof core-shell-type spin structure?

Research area: Materials

This proposal is a new proposal

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Samples: Ni50Mn33In17

Instrument	Requested days	Allocated days	From	To
D33	6	3	03/02/2017	06/02/2017

Abstract:

The aim of our proposal is to study the purely magnetic microstructure of Ni-Mn-In Heusler alloys on a mesoscopic microstructural length scale (1-300 nm) by means of magnetic SANS. In order to disentangle the nuclear coherent scattering signal from the magnetic contribution, we will make use of the recently developed so-called POLARIS technique (1D polarization analysis). By means of POLARIS, it becomes possible to access all three magnetization Fourier components as a function of temperature and applied magnetic field. We are not aware that such an experiment has been carried out on Ni-Mn-In Heusler alloys, and we believe that, besides improving our understanding of the POLARIS technique, it will provide fundamental insights into the underlying mechanism of magnetic SMA; in particular, we will be able to prove or disprove a recently proposed core-shell-type spin structure for this type of material.

Magnetic SANS study of shell-ferromagnetism in $Ni_{50}Mn_{45}In_5$ Heusler alloy

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A new functional property in off-stoichiometric $Ni_{50}Mn_{45}In_5$ Heusler alloy has been recently observed.[1] The compound, when annealed at high temperatures in a range between 650 K and 750 K under application of a magnetic field, decomposes into $Ni_{50}Mn_{25}In_{25}$ nano-precipitates embedded in a NiMn matrix. The precipitates are paramagnetic (PM) at the annealing temperature, whereas the matrix is antiferromagnetic (AF). The spins at the interface with the NiMn matrix align with the field during their growth and become strongly pinned in the field direction during annealing, whereas the core spins become PM. This effect of a PM precipitate with a ferromagnetic (FM) shell (shell-ferromagnetism) has been postulated, but the actual spin microstructure of such samples is still unclear. It is the aim of the present experiment to obtain information about the microstructure of $Ni_{50}Mn_{45}In_5$ Heusler alloys by means of polarized small-angle neutron scattering (SANS) technique.

$Ni_{50}Mn_{45}In_5$ samples were prepared by arc melting of high-purity elements (99.9%) and were annealed under Ar atmosphere at 1073 K in sealed quartz tubes for 5 days for homogenization purpose; the specimens were then quenched in water at room temperature. The initial compositions were determined by using energy dispersive x-ray analysis (EDX). To check for sample homogeneity, EDX spectra were collected from seven different areas. Two samples have been annealed in a vibrating sample magnetometer (VSM) under a magnetic field of 5 T at a temperature of 700 K during 12 h and at 650 K during 6 h. In the following, we denote them by "700 K" and "650 K" samples, respectively. The spins at the interface between the matrix and the precipitates align with the direction of the applied field $\mathbf{T}$ and remain strongly pinned in this direction after annealing.[1] Therefore, it is worth noting that the samples may be magnetically textured and the SANS experiments were correspondingly performed for two possible orientations of the applied field $\mathbf{H}_0$ with respect to the texture axis $\mathbf{T}$. A third sample is used as a reference sample and we denote it by "initial state".

The SANS experiment was carried out at the instrument D33 at the Institut Laue-Langevin (ILL), Grenoble, France. The measurements on the 650 K and 700 K annealed samples were made using both polarized and unpolarized incident neutrons with a mean wavelength of $\lambda = 6\,$Å, $\Delta\lambda/\lambda \sim 10\%$ (FWHM), and for a q-range of about $0.035\,\mathrm{nm}^{-1} \leq q \leq 1.5\,\mathrm{nm}^{-1}$. The magnetic field was applied perpendicular to the incident neutron beam ($\mathbf{H}_0 \perp \mathbf{k}_0$) and either parallel to the texture axis ($\mathbf{H}_0 \parallel \mathbf{T}$) or perpendicular to it ($\mathbf{H}_0 \perp \mathbf{T}$). Neutron data were recorded by first applying a large positive field of 8 T, and then reducing the field following the magnetization curve (compare Fig. 1). All data were collected at room temperature. SANS data reduction (correction for background scattering, transmission, detector efficiency, spin-leakage) was carried out using the GRASP software package.[2]

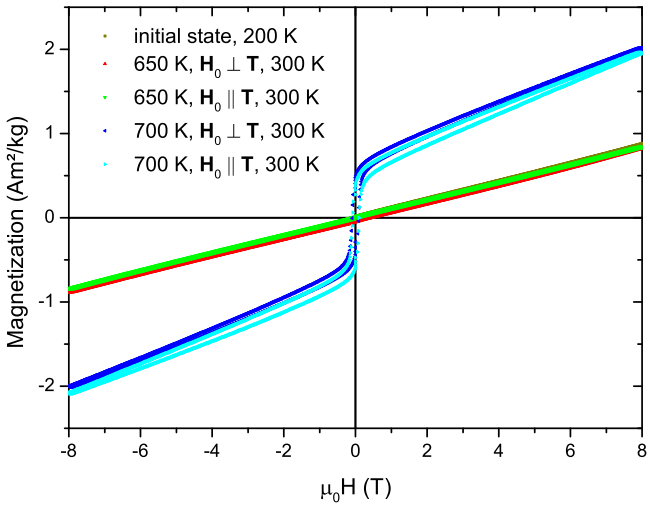

FIG. 1. Room-temperature magnetization curves of the 650 K and 700 K samples for two directions of the applied field ($\mathbf{H}_0 \perp \mathbf{T}$ and $\mathbf{H}_0 \parallel \mathbf{T}$). The magnetization curve of the initial state sample was recorded at $T = 200$ K.

For the scattering geometry where the applied magnetic field (assumed to be parallel to the $\mathbf{e}_z$ direction of a Cartesian laboratory coordinate system) is perpendicular to the incident neutron beam ($\mathbf{H}_0 \perp \mathbf{k}_0$), the elastic unpolarized SANS cross section $d\Sigma/d\Omega$ at momentum-transfer vector $\mathbf{q}$ can be written as[3]

$$\frac{d\Sigma}{d\Omega}(\mathbf{q}) = \frac{8\pi^3}{V} b_H^2 \Big(b_H^{-2} |\widetilde{N}|^2 + |\widetilde{M}_x|^2 + |\widetilde{M}_y|^2 \cos^2\theta + |\widetilde{M}_z|^2 \sin^2\theta - (\widetilde{M}_y \widetilde{M}_z^* + \widetilde{M}_y^* \widetilde{M}_z) \sin\theta\cos\theta \Big), \quad (1)$$

where $\mathbf{q}$ is the scattering or momentum-transfer vector, V is the scattering volume, $b_H = 2.91 \times 10^8\,\mathrm{A^{-1}m^{-1}}$ relates the atomic magnetic moment to the Bohr magneton, and $\widetilde{N}(\mathbf{q})$ and $\widetilde{\mathbf{M}}(\mathbf{q}) = \{\widetilde{M}_x(\mathbf{q}), \widetilde{M}_y(\mathbf{q}), \widetilde{M}_z(\mathbf{q})\}$ denote, respectively, the Fourier coefficients of the nuclear scattering-length density and of the magnetization

$\mathbf{M}(\mathbf{r})$; θ represents the angle between $\mathbf{H}_0$ and $\mathbf{q}$ so that $\mathbf{q} \cong q\{0, \sin\theta, \cos\theta\}$; the asterisks "$*$" mark the complex-conjugated quantity and the atomic magnetic form factor (in the expression for b_H) is approximated to unity since we are dealing with forward scattering.

Assuming a perfect neutron optics and neglecting nuclear spin-incoherent SANS, the spin-flip SANS cross section of a bulk ferromagnet can be written as[3]

$$\frac{d\Sigma^{\pm\mp}}{d\Omega}(\mathbf{q}) = \frac{8\pi^3}{V} b_H^2 \Big(|\widetilde{M}_x|^2 + |\widetilde{M}_y|^2 \cos^4\theta + |\widetilde{M}_z|^2 \sin^2\theta \cos^2\theta - (\widetilde{M}_y \widetilde{M}_z^* + \widetilde{M}_y^* \widetilde{M}_z) \sin\theta \cos^3\theta \Big) . \quad (2)$$

The first superscript (e.g."+") that is attached to $d\Sigma/d\Omega$ in Eq. (2) refers to the spin state of the incident neutrons, whereas the second one (e.g."−") specifies the spin state of the scattered neutrons. Polarization-dependent chiral scattering terms were neglected in Eq. (2).

Figure 2(a) displays the radially-averaged SANS cross sections for the initial state, 650 K, and 700 K samples in the remanent state. The initial state and 650 K sample exhibit similar magnetization (Fig. 1) and scattering curves. When the sample is annealed at 700 K, the scattering curve changes substantially: a broad hump at $q \cong 0.15$ nm^{-1} becomes visible, which we interpret as the signature of ferromagnetic precipitates. Moreover, all the scattering curves exhibit significant additional scattering contribution at the smallest momentum-transfers, which is related to the presence of large-scale structures that cannot be resolved by our experiment.

In Fig. 2(b) we show the normalized real-space correlation functions of the three data sets from Fig. 2(a). The horizontal line $c(r) = \exp(-1)$ and its intersections with the respective curves yield the values of the (structural and magnetic) correlation length l_C. We see that l_C decreases when the annealing temperature increases (initial state: $l_C \cong 65$ nm; 650 K: $l_C \cong 50$ nm; 700 K: $l_C \cong 35$ nm). The initial state sample is expected to exhibit the most homogenous microstructure of all the three samples, with a low volume fraction of defects corresponding to a relatively large correlation length. Since the annealing treatment results in microstructural transformations (e.g., in the precipitation of second-phase magnetic particles), one expects l_C to decrease with increasing annealing temperature.

Figures 3(a) and (b) display the spin-flip SANS cross section $d\Sigma^{+-}/d\Omega$ at $\mu_0 H_0 = 1$ T for the 650 K and 700 K samples, respectively. The 650 K sample scatters very weakly and the cross section exhibits no pronounced angular anisotropy. By contrast, the $\sin^2\theta\cos^2\theta$-type anisotropy observed for the 700 K sample suggests the existence of a significant ferromagnetic component [compare Eq. (2)]. These observations are in agreement with the unpolarized data, *i.e.*, the magnetic scattering is very weak for the 650 K sample and more pronounced for the 700 K sample. Figure 3(c) and (d) show the difference

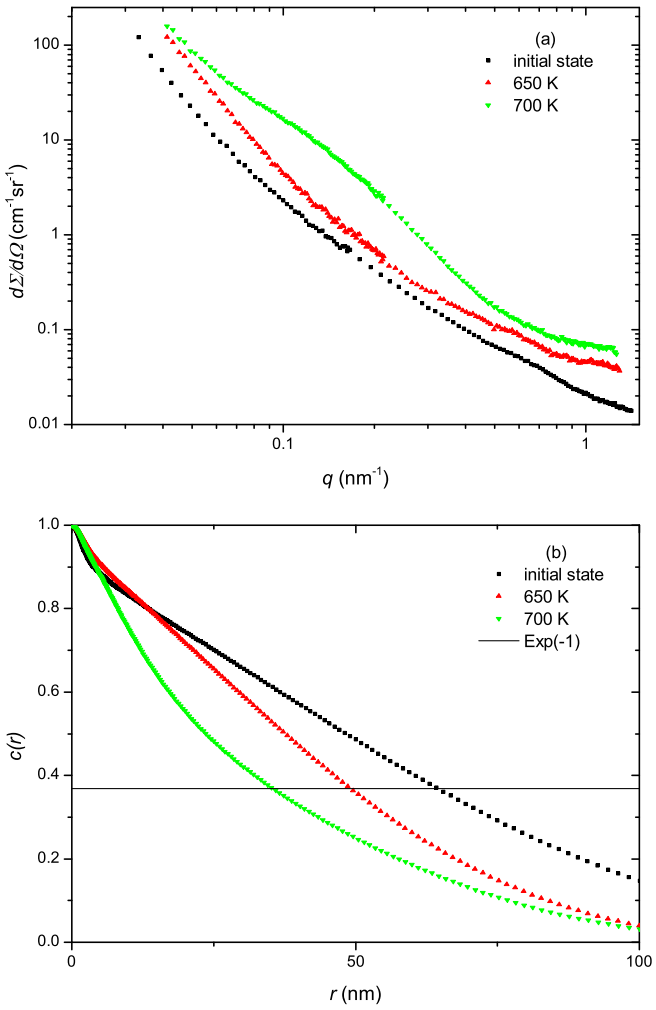

FIG. 2. (a) Radially-averaged unpolarized SANS cross sections at the remanent state for the initial state, 650 K, and 700 K samples (log-log scale). Note that the data of the initial state sample have been rescaled by a factor of 1/10920. (b) Same as (a) for the corresponding normalized correlation functions.

between the non-spin-flip cross section, *i.e.*, the nuclear-magnetic interference terms, at $\mu_0 H_0 = 1$ T for the 650 K and 700 K samples, respectively. The very weak intensity observed for the 650 K sample suggests again that the magnetic scattering is weak, whereas the $\sin^4\theta$-type anisotropy of the 700 K sample suggests a strong ferromagnetic component.

In summary, the results of our neutron study reveal a possible precipitation process in the magnetic field annealed $Ni_{50}Mn_{45}In_5$ Heusler samples. Further data analysis using real-space techniques (e.g., Lorentz TEM) will help in identifying the nature (size and shape) of the precipitates.

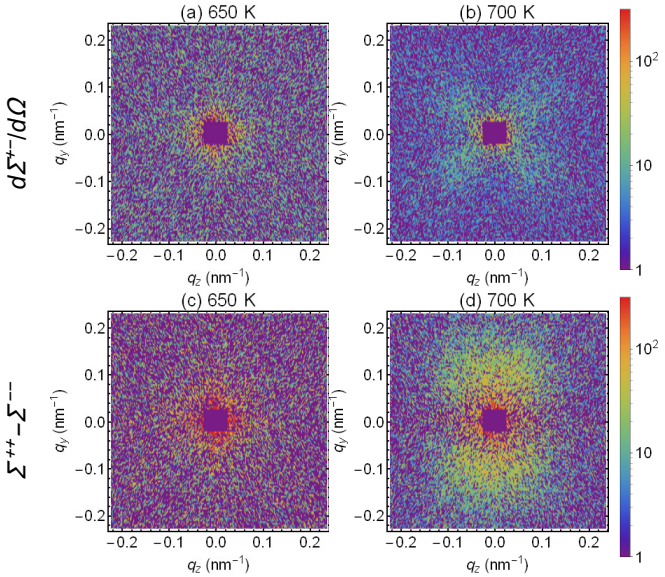

FIG. 3. Spin-flip SANS cross sections $d\Sigma^{+-}/d\Omega$ in the plane of the two-dimensional detector for the (a) 650 K and (b) 700 K samples (logarithmic color scale). Difference between non-spin-flip SANS cross sections, $d\Sigma^{++}/d\Omega - d\Sigma^{--}/d\Omega$, for the (c) 650 K and (d) 700 K samples. All the data are shown for $\mu_0 H_0 = 1$ T.

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