# Experimental Report



**Proposal:** **5-31-2197** **Council:** 4/2012

**Title:** Neutron diffraction study in highly concentrated Mn-based nanostructured alloys for potential permanent magnet applications

**This proposal is a new proposal**

**Researh Area:** Materials

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**Local Contact:** PUENTE ORENCH INES

**Samples:** Ag100-xMn

| Instrument | Req. Days | All. Days | From | To |
|---|---|---|---|---|
| D1B | 3 | 3 | 04/12/2012<br>08/12/2012 | 06/12/2012<br>09/12/2012 |

**Abstract:**

Mn-based alloys containing high Mn concentrations are under investigation for potential permanent magnet applications. Results show remarkable exchange bias values in all the highly concentrated alloys of around 10-15 kOe at low temperatures. Such promising magnetic features are related to the magnetic structure of the samples, tentatively attributed to a cluster glass behavior. XRD experiments confirm the existence of two-phase magnetic systems. It is proposed to carry out 3 days of experiments at D1B to study better the structural and magnetic structure of these two phases.

# Neutron diffraction study in highly concentrated Mn-based nanostructured alloys for potential permanent magnet applications (5-31-2197)

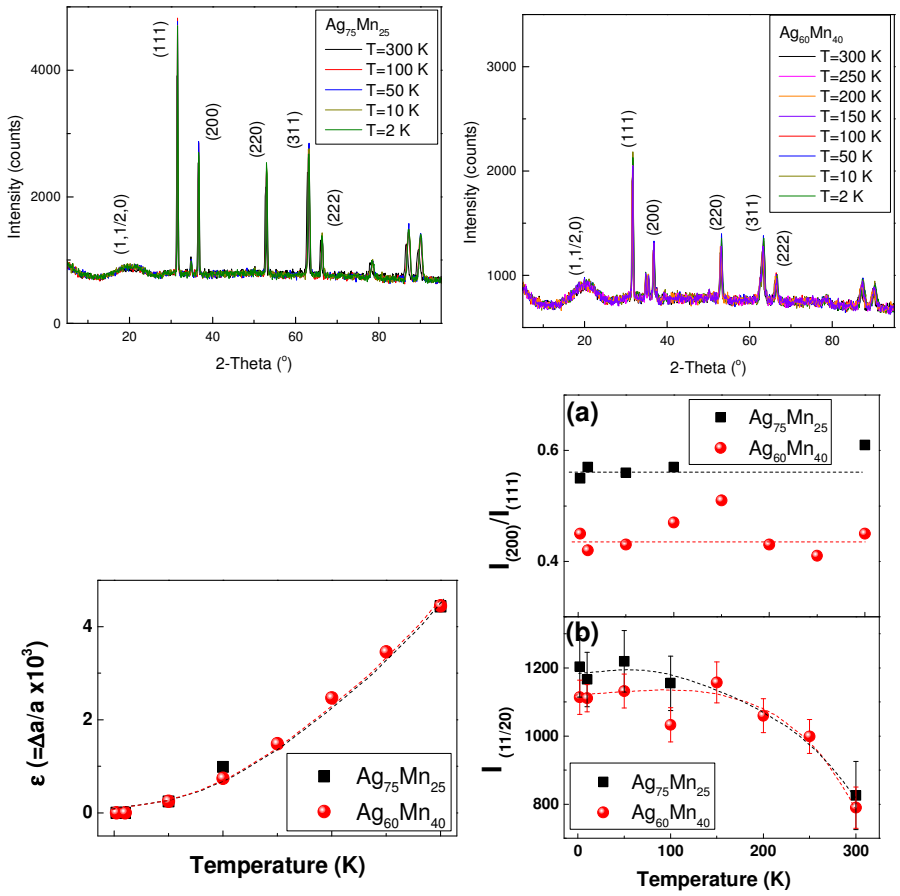
**Experimental.** Neutron diffraction experiments were performed in the high-flux two-axis D1B diffractometer at the Institut Laue-Langevin (ILL). Diffraction patterns at selected temperatures, from 2 to 300 K, were collected using a calibrated wavelength of $\lambda$ = 1.2899 Å. The $NM_{100-x}Mn_x$ ribbons where cut in very small parts, sealed into a 6 mm cylindrical vanadium container and placed inside a cryostat. Crystal structure was refined by the Rietveld method using the Fullprof Suite of programs.[1]

- **AgMn**

Neutron diffraction experiments were achieved at a broad range of temperatures in order to determine possible magnetic ordering (from 2 to 300K for $Ag_{75}Mn_{25}$ and $Ag_{60}Mn_{40}$, respectively). The diffraction pattern at 300K (paramagnetic state of the alloys) was used for Rietveld refining the nuclear structure (Fm-3m), the stoichimiometry of the alloy coincide which this obtained through EDX measurements. Different positions of the Mn atoms have been tested in the structural model, but the best fit is obtained when Mn atoms are incorporated at random in the Ag lattice. As already observed from the X-ray diffraction experiments, Mn incorporation in the lattice causes a reduction in the cell parameter. The thermal expansion coefficient, $\varepsilon = \Delta a/a = [a(T)–a(2\ K)]/a(2\ K)$, was obtained from the diffraction scans at different temperatures, yielding a value of the thermal expansion coefficient of around $\varepsilon \approx 4\times10^{-3}$ at room temperature, respect to the measurements at 2 K. Results show an evolution similar to other metallic Mn-based alloys.[2]

In Mn-based alloys, additional Bragg peaks indicating long-range antiferromagnetic (AF) ordering (like (110) peak at around 25°, or the (201) peak around 40°) may appear in the neutron diffraction scans, evolving with temperature below the ordering temperature ($T_N$). No additional Bragg peaks, compared to the x-ray diffraction patterns, are present in the measurements, suggesting the absence of a commensurate long-range AF ordering in these AgMn alloys. The intensity ratio $I_{(200)}/I_{(111)}$ results to be very different for the alloys $Ag_{75}Mn_{25}$ and $Ag_{60}Mn_{40}$, not varying significantly with temperature (the ratio for $Ag_{75}Mn_{25}$ is around 0.56, whereas for $Ag_{60}Mn_{40}$ is about 0.44). A possible interpretation of the different intensity ratio $I_{(200)}/I_{(111)}$ may be provided accounting for the increasing number of Mn-Mn nearest neighbors with increasing concentration of Mn (it is well known that the scattering length of Mn is negative, and small in comparison with the Ag atom, which will result in (002) plane reflections with a weaker intensity).

Finally, both samples exhibit a broad peak at around $2\theta \approx 20°$, associated with a diffuse scattering feature from reflections of the (1 ½ 0) planes, more narrow in the $Ag_{60}Mn_{40}$ sample than that displayed by the $Ag_{75}Mn_2$ sample, in agreement with previous results for CuMn at such range of Mn concentration.[3] This feature is hardly visible with X-ray because the large intensity difference with the Bragg´s diffracted peaks. A gradual decrease of the diffraction intensity with increasing temperature is observed in all the Bragg peaks and diffuse peak throughout the whole range. The fact that the diffuse peak is present throughout the whole range of temperatures, even above $T_B$, following a variation similar to those of the (111) and (200) atomic scattering peaks, may suggest a predominant nuclear nature of this diffraction feature, in agreement with extensive previous literature.[4,5] All diffuse and Bragg peaks experiment a decrease with increasing temperature, likely caused in part to Debye-Waller thermal effects.

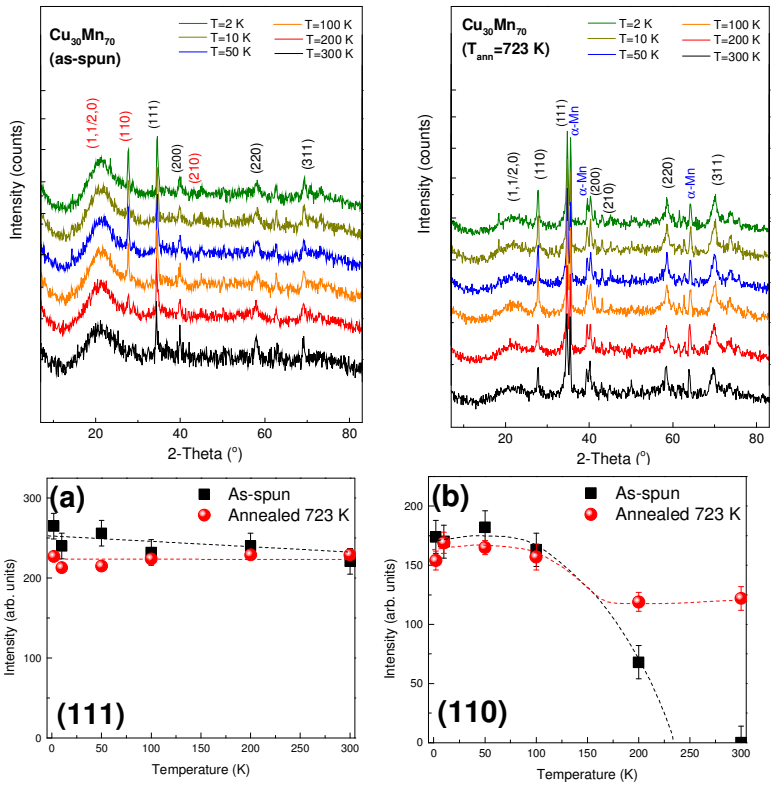



- **<u>CuMn</u>**

The neutron diffraction patterns reproduce the γ-CuMn phase peaks observed by x-ray diffraction. However, an analysis of the structural features was hampered by the very low Bragg peak intensity, since relative atomic proportions are similar to that of a null-matrix alloy. In this null-matrix alloy configuration, Bragg peaks present a weak intensity, highlighting the presence of the diffuse contribution. At first glance results of the annealing reveal, that the (1½0) diffuse peak, associated with atomic-magnetic short range order (SRO), becomes much smaller in intensity.

Besides the structural (nuclear) peaks, an additional narrow peak at around $2\theta \sim 28°$, associated with a (110) reflection, a well-known signature of long-range AF ordering, is observed. The evolution of the intensity of this peak with temperature, however, is different in both samples. A constant intensity is displayed up to around 100 K, with a progressive decrease at higher temperatures. However, the (110) peak, that disappears in the as-spun sample, persists in the annealed ribbons throughout the range of temperatures analyzed. This is a clear signature of the presence of an additional phase with AF ordering and with a Neel temperature above 300 K.

Also, the as-spun sample shows a broad peak at $2\theta \sim 21°$, identified as the diffuse (1½0) peak. The observation of this feature along the whole range of temperatures, even at $T > T_B$ may suggest a predominance of the atomic (nuclear) component. However, this peak is not observed in the x-ray diffraction patterns, so a non-negligible contribution of the magnetic scattering component should not be ruled out. On the other hand, the diffuse peak practically disappears in the annealed sample.




- **Origin and nature of (1 ½ 0) diffuse peak.**

Previous neutron scattering experiments reveal strong magnetic correlations of both FM and AF character appearing at temperatures several times higher than the temperature of spin-freezing. It was suggested that the diffuse peak in Mn-rich alloys possesses a predominant magnetic component, since its intensity increases with increasing temperature reaching a maximum at the Neel temperatures of the alloys, whereas for Mn-poorer alloys (< 69 at.% Mn), the peak is mainly due to atomic short-range order, with a monotonous decrease of the intensity with increasing temperature throughout the whole temperature range. This interpretation is supported by the decrease of the diffuse peak intensity in Mn-rich γ-CuMn alloys simultaneously with increasing (110) Bragg peak (signature of long-range AF order) at high Mn concentrations.[5,6] A complex atomic and magnetic short-range ordering nature was claimed in γ-CuMn and γ-NiMn alloys.[7,8] Alloys with low Mn concentration ($x \leq 40\%$) tend to form atomic short range arrangement and magnetic short range ordering of incommensurate spin density wave type, forming a largely disordered state characterized by a diffuse concentration wave with wavevector $Q_a = (1½0)$.[9]

## References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