Experimental report

25/07/2023

Proposal: 5-31-2945 **Council:** 10/2022

Title: Fe100-xRhx alloys with x near 50: evolution of the crystal and magnetic structures on the first-order magnetostructural transition

Research area: Materials

This proposal is a new proposal

Main proposer: Pablo ALVAREZ

Experimental team: Pablo ALVAREZ
Javier LOPEZ GARCIA

Local contacts: Ines PUENTE ORENCH

Samples: Fe100-xRhx (x = 50, 51)

Instrument	Requested days	Allocated days	From	To
D1B	3	2	19/06/2023	21/06/2023

Abstract:

Binary FeRh alloys with a chemical composition close to equiatomic exhibit the highest adiabatic temperature change ever reported. The effect is associated with the coupled first-order magnetoelastic phase transition, which is accompanied by a change in the magnetic structure from antiferromagnetic (AFM) to ferromagnetic (FM). We have analyzed two induction melted and thermally annealed bulk Fe100-xRhx alloys with x=50 and 51, which show well-different phase transition characteristics: the first-order magnetostructural transition for 49:51 samples is quite abrupt and is accompanied by a magnetization change ¿M of 122 Am2kg-1, while it spreads over a wide temperature interval and ¿M fluctuates around 116 Am2kg-1 for the 50:50 one. Consequently, both samples show magnetocaloric properties that are very different. We propose a neutron thermo-diffraction experiment in D1B to investigate how the crystallographic and magnetic structures as well as their degree of coupling evolve with the temperature through both the AFM-FM and FM-AFM transitions. The latter will provide a better understanding of the correlation between the observed magnetostructural and magnetocaloric properties.

Binary Fe100-xRhx alloys with $48 \leq x \leq 54$ at. % exhibit a giant magnetocaloric effect (GMCE) near room temperature, exhibiting the greatest adiabatic temperature changes $|\Delta T_{ad}|^{max}$ ever reported [1]. Due to the large amount of heat released by Fe-Rh compounds upon the adiabatic application of an external magnetic field, they have been proposed as robust candidates for several low-mass applications in the field of medicine such as controllable drug delivery and release of bioactive substances, and local heating of neoplasms [2]. The GMCE arises from a magnetoelastic phase transition induced by a first-order phase transition from antiferromagnetic (AFM, α'') to ferromagnetic (FM, α') states (and vice versa) of the ordered CsCl-type crystal structure (also known as B2), accompanied by a volume expansion (reduction) of the unit cell by approximately 1% on heating (cooling) [3].

We have analyzed the magnetic phase transition in induction-melted $Fe_{100-x}Rh_x$ alloys (x = 50 and 51) and thermally annealed at 1000°C for 48 h. To this end, we measured the thermal dependence of both the heat released and absorbed by the sample, as well as the low magnetic field dependence of magnetization. We have found the FOMST transition for 49:51 sample occurring in about 3 K, being accompanied by a magnetization change ΔM of 122 Am^2kg^{-1}. In contrast, the 50:50 alloy presents a FOMST that spreads over a temperature interval of around 25 K with ΔM fluctuating around 116 Am^2kg^{-1} [4]. We also conducted X-ray diffraction (XRD) experiments, although the obtained information is limited to a thin surface layer of the bulk because FeRh alloys are difficult to pulverize due to their mechanically hardness. Besides, when pulverized, the stress produced triggers the transformation of the chemically ordered CsCl-type crystal structure into the paramagnetic fcc gamma phase [5]. Moreover, the structural information provided by XRD analysis often contradicts the information provided by magnetization measurements [4-5]. In this sense, the allocated bean time for neutron diffraction experiment is crucial for studying the phase transition and magnetic structure of these alloys.

The primary objective of this experiment was to comprehensively investigate the magnetoelastic phase transition through Neutron (ND) and X-ray powder diffraction experiments, along with magnetic measurements, aiming to discern the coupling features of the interatomic distances and magnetic structure. Given the time constraints (2 days of beam time were allocated), we opted to use a crio-furnace and focus on studying the evolution of the cell parameters and magnetic structure of the antiferro- and ferromagnetic phases at temperatures below 500 K (the Curie temperature is around 650 K). Neutron diffraction patterns were collected during two different temperature ramps, both in heating from 10 to 500 K and in cooling from 500 to 10 K. The wavelength utilized was $\lambda = 2.52$ Å, and the angular range (2θ) between 0º and 128º, with the range 83-88º discarded due to the banana detector issues. In preliminary measurements, a high sample texture was detected, so we attempted to mitigate it by rotating our bulk samples around the cane axis during the neutron diffraction pattern collection by installing a motor in the experimental configuration to simulate a powder. However, a malfunction of the motor prevented us from successfully implementing this approach. Nonetheless, the motor allowed us to rotate the sample at discrete steps to find a position where the texture was less predominant and then acquire the ND patterns.

The preliminary analysis of the data has provided us with the evolution of the cell parameter with the temperature, offering valuable insights into the magnetoelastic phase transition. The observed abrupt evolution of the lattice parameter in the sample $Fe_{49}Rh_{51}$ and broad in the $Fe_{50}Rh_{50}$ (see Fig. 1) agrees well with the behavior of the magnetization as a function of the temperature. These results will be correlated with the previously conducted XRD experiment [6]. These findings will be included in an article that is nearly ready for submission. Additionally, we are currently investigating the magnetic structure (Fig. 2) at both low (AFM phase) and at higher temperatures (FM phase).

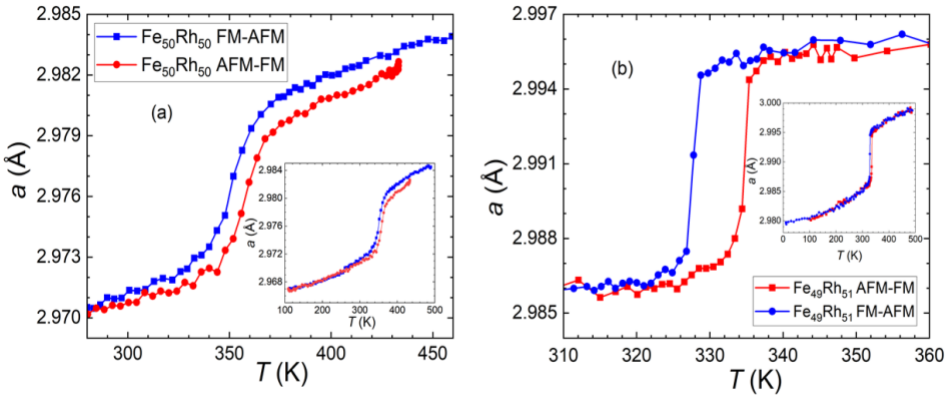

Fig. 1. Dependence of the Cell parameter with the temperature in heating and cooling (a) $Fe_{50}Rh_{50}$ and (b) $Fe_{49}Rh_{51}$.

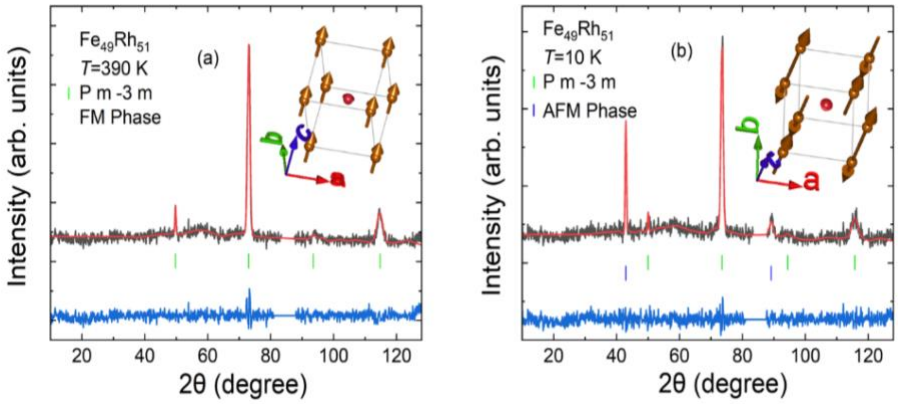

Fig.2. Neutron diffraction pattern (4 min recorded) of the $Fe_{49}Rh_{51}$ alloy and a Rietveld refinement in the (a) FM phase at 390 K and (b) AFM phase at 10 K.

REFERENCES

[1] M.P. Annaorazov et al., Alloys of the Fe-Rh system as a new class of working material for magnetic refrigerators, Cryogenics 32 (1992) 867-872.
[2] A.P. Pyatakov, Y.I. Spichkin, A.M. Tishin, V.I. Zverev, A magnetic field controllable implantable device and a method of controlled drug release therefrom. UK patent GB 2520960, date of patent 10.06.2015.

[3] L.H. Lewis, C.H. Marrows, S. Langridge, Coupled magnetic, structural, and electronic phase transitions in FeRh, J. Phys. D: Appl. Phys. 49 (2016) 323002.
[4] M.L. Arreguin Hernández, Master Science thesis, Magnetostructural transition in bulk Fe100-xRhx (x= 50, 50.5 y 51) alloys and rapidly quenched Fe49.5Rh50.5 alloy ribbons, IPICyT, Mexico, July 11, 2019.
[5] A. Chirkova et al., The effect of the microstructure on the antiferromagnetic to ferromagnetic transition in FeRh alloys, Acta Materialia 131 (2017) 31-38
[6] C.F. Sánchez-Valdés et al., The effect of cooling rate on magnetothermal properties of Fe49Rh51, J. Magn. Magn. Mater. 498 (2020) 166130.