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## Defects structure characterization of NiMnGa alloys by PALS

David Merida<sup>1</sup>, Jose Angel Garcia<sup>1</sup>, Fernando Plazaola<sup>2</sup>, Vicente Sanchez-Alarcos<sup>3</sup>, Jose Ignacio Pérez-Landazábal<sup>3</sup> and Vicente Recarte<sup>3</sup>

<sup>1</sup>Fisika Aplikatua II Saila, Euskal Herriko Unibertsitatea UPV/EHU, p.k. 644, 48080 Bilbao, Spain

<sup>2</sup>Elektrizitate eta Elektronika Saila, Euskal Herriko Unibertsitatea UPV/EHU, p.k. 644, 48080 Bilbao, Spain

<sup>3</sup>Departamento de Física, Universidad Pública de Navarra, Campus de Arrosadia, 31006 Pamplona, Spain

E-mail: david.merida@ehu.es

**Abstract.** We have studied the behaviour of defects in off-stoichiometric Ni-Mn-Ga ferromagnetic shape memory alloys by means of positron lifetime spectroscopy. The measurements presented in this work have been performed in six ternary alloys. The studied samples cover a large composition range. Positron experiments have been performed at room temperature after subsequent isochronal annealing at different temperatures up to a maximum temperature of 700°C. Results show a large variation of the average positron lifetime value with the isochronal annealing temperature in three of these samples, with significant differences between them. In the other three, the response is quite different. The results are discussed in terms of different types of positron trapping defects and their evolution with the annealing temperature. The present work shows a high dependence of recovery behaviour with composition in NiMnGa ferromagnetic shape memory alloys.

### 1. Introduction

Since giant magnetic-field-induced strain (MFIS) was first reported on Ni-Mn-Ga ferromagnetic shape memory alloys (FSMA) by Ullakko et al. [1], a great amount of work has been performed to understand and improve the system in order to be implemented in practical devices [2]. The main drawbacks are the high brittleness, the low values of the martensitic transformation (MT) and the Curie temperatures of Ni-Mn-Ga alloys. These limitations have stimulated the research of new ferromagnetic shape memory alloys having better mechanical properties. Indeed, several studies have been performed to improve the mechanical and thermal properties [3].

Different techniques have been used to analyze diverse properties of Ni-Mn-Ga alloys; however, very little work has been performed to study the role of vacancies in the martensitic transformation [4-5]. Positron annihilation spectroscopy is a very powerful technique to investigate vacancy-type defects in metals [6]. We have used positron annihilation spectroscopy measurements to study the behaviour

<sup>1</sup> To whom any correspondence should be addressed.



of vacancy-type defects in different composition off-stoichiometry of Ni-Mn-Ga polycrystalline alloys. Positron lifetime experiments have been performed at room temperature after subsequent isochronal annealing up to 700°C.

## 2. Experimental

Polycrystalline ingots of Ni<sub>2</sub>MnGa were prepared from high purity elements by arc melting under protective Ar atmosphere. The ingots were homogenized in vacuum quartz ampoules at 1000 °C for 24 hours. Samples for measurements were obtained from discs previously cut from the center of the ingots by slow speed diamond saw. These discs were used for positron lifetime measurements. Subsequent annealing treatments of 30 minutes at 900 °C followed by quenching into ice water were performed on the alloys in a vertical furnace.

For positron lifetime measurements a fast system with a resolution of 240 ps was used and a conventional <sup>22</sup>Na source on a kapton foil was employed as the positron source. All lifetime spectra were analyzed after subtracting a constant source contribution. The statistic of each spectrum was always better than 1.6 million counts. For the isochronal annealing the same heating/cooling rate of 10 K/min was used. The points in each positron lifetime curve correspond to the average obtained after 5 measurements. For all of the results the error of the measured positron lifetimes is within error bars showed in the figures. B samples exhibit structural modulation; however, A samples do not show modulation [7]. The compositions of the six samples, determined by EDX, are shown in Table 1.

Table 1. Composition of the modulated and non-modulated samples used in the measurements.

	Ni	Mn	Ga
<b>A1</b>	51.6	29.3	19.1
<b>A2</b>	55.8	19.7	24.5
<b>A3</b>	53.9	25.4	20.7
<b>B1</b>	50.1	27.8	22.2
<b>B2</b>	48.7	26.2	25.1
<b>B3</b>	53.5	20.8	25.7

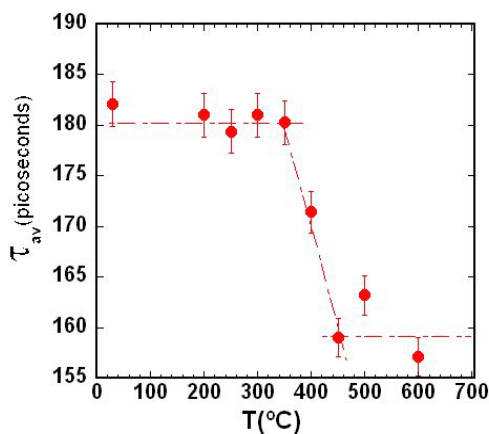
## 3. Results and discussion

Figure 1 shows the behaviour of the average positron lifetime ( $\tau_{av}$ ) as a function of isochronal annealing temperature for sample A1. The first value of  $\tau_{av}$  amounts to about 182 ps and corresponds to the sample as quenched from 900°C. Only one positron lifetime component is present in the spectrum indicating that all positrons are annihilating from one positron state, whose lifetime near 182 ps. The second point corresponds to the first annealing after the quench, performed at 200°C. Isochronal annealing performed between 200°C and 350°C do not change within the experimental error the value of  $\tau_{av}$  measured after the quench. This lifetime value is typical of positrons annihilating from vacancies in metals [8]. Between 350°C and 450°C  $\tau_{av}$  decreases around 20 ps, down to a value near 160 ps, where it remains up to the highest measured isochronal annealing temperature. A second component is needed for a correct fit of the last spectra. The decrease in  $\tau_{av}$  indicates the elimination of thermal vacancies retained during the quench. The fact that in the last points there are two components indicates that a total elimination of vacancies is not reached. There can be two reasons to explain this behaviour: 1) the presence of constitutional vacancies, which cannot be eliminated by thermal treatments, 2) the used heat treatment is not the adequate one to obtain the elimination of vacancy type defects up to levels below the sensitivity of the PALS technique.

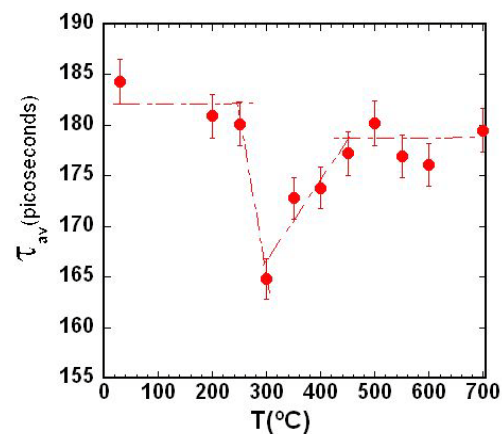
Figure 2 shows the behaviour of the  $\tau_{av}$  as a function of isochronal annealing temperature for sample A2. The first three points remain near 182 ps; however, at 300°C  $\tau_{av}$  decreases abruptly to 165 ps. For isochronal annealing temperatures between 300°C and 500°C  $\tau_{av}$  increases monotonically up to around 178 ps, where it remains constant up to the highest measured isochronal annealing temperature. There are two significant differences in the behaviour of the previous A samples. The first one is the

shift of about 100 °C on the starting of  $\tau_{av}$  decrease from around 180 ps (the shift amounts to about 150 °C in reaching the minimum of  $\tau_{av}$ ). The second one is the lifetime increase observed in sample A2 for annealing temperatures above 300 °C. The first difference can be due to different migration energies of the involved vacancy type defects. The  $\tau_{av}$  increase observed in the isochronal annealing of sample A2 suggests that new thermal vacancies appear at temperatures above 300 °C. That is to say, the cooling rate of 10°C/min is too fast to eliminate the newly created thermal vacancies. The observed significant differences indicate that the migration energies of the vacancy type defects involved in samples A1 and A2 are quite different. It is difficult to imagine such large differences caused by the same vacancy type defect in samples with identical structure but different composition. Therefore, one may conclude that the observed differences are caused by different vacancy type defects in the structure of samples A1 and A2. Moreover, table 1 shows that A1 sample is poor in Ga and sample A2 in Mn, which suggests that Ga vacancies are involved in the observed behaviour of sample A1 and Mn vacancies in the one of sample A2.

Figure 3 shows the behaviour of  $\tau_{av}$  as a function of isochronal annealing temperature for sample A3. Up to 300 °C  $\tau_{av}$  remains constant at around 183 ps. It decreases between 300°C and 450°C down to around 170 ps, where it remains quite constant. This behaviour is quite similar to that of A1 sample (poor in Ga, too), but with a higher remaining vacancy content.



**Figure 1.**  $\tau_{av}$  as a function of the isochronal annealing temperature for A1 sample.

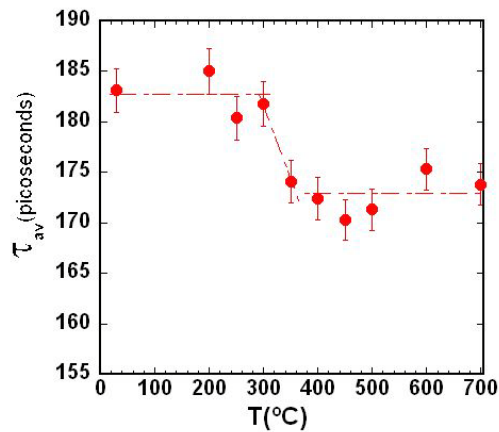


**Figure 2.**  $\tau_{av}$  as a function of the isochronal annealing temperature for A2 sample.

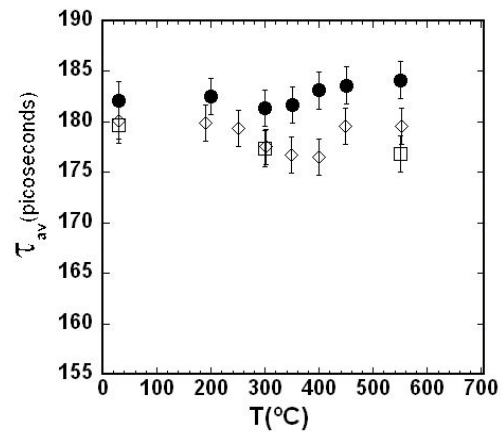
Figure 4 shows the behaviour of  $\tau_{av}$  as a function of isochronal annealing temperature for B1, B2 and B3 samples. The behaviour of  $\tau_{av}$  in these samples is very different to the previous ones. B1 sample shows only a valley between 250 °C and 450 °C, but the overall  $\tau_{av}$  decrease amounts only to about 3 ps. It is not possible to decompose the spectra in all the studied temperature range and the positron lifetime value of 180 ps, measured below 250 °C, is about the same value measured above 450 °C. So, positrons are annihilating in saturation from vacancies below 250 °C and above 450 °C. Therefore, the valley observed in the temperature range 250-450 °C cannot be understood as the elimination of only one type of vacancies.

The value of  $\tau_{av}$  measured in B2 sample remains almost constant and in saturation in the studied temperature range. In the case of B3 sample only three points have been measured to confirm the behaviour of the other two samples. In the case of B samples, modulated ones the vacancy content is very high in all the isochronal annealing temperature range.

There exists a clear difference between the results in A and B samples. In A samples, a clear elimination of vacancies is observed, while in the modulated ones, such elimination is not observed at all. This means that the behaviour of vacancies in these two kinds of samples is very different.



**Figure 3.**  $\tau_{av}$  as a function of the isochronal annealing temperature for A3 sample.



**Figure 4.**  $\tau_{av}$  as a function of the isochronal annealing temperature for B1 (open rhombus), B2 (full circle) and B3 samples (open squares).

#### 4. Conclusion

The behaviour of vacancy type defects in off-stoichiometry polycrystalline  $\text{Ni}_2\text{MnGa}$  ferromagnetic shape memory alloys has been studied by measuring the effect of the thermal treatment. To analyze the effect of the composition on the isochronal annealing behaviour six different samples, covering a large composition range, were studied. Positron lifetime measurements show a clear and significant difference in the behaviour of positron traps (vacancies) in the two A and B family samples. In B samples the vacancy content remains above the saturation limit in the studied temperature range. However, in the case of A samples there is a clear elimination of vacancies. Within samples of A type a clear difference in the behaviour of the positron traps is measured, too. The obtained results suggest that the type of vacancy present in the sample, after quenching, depends on the composition of the alloy. Indeed, the recovery state can be shifted as much as 150 °C.

#### Acknowledgments

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