Structure determination of Fe-Al-Ge alloys

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Abstract. We studied the crystalline structure of Fe - 8at.%Al - 4at.%Ge alloy between 300 and 1300 K and its relation to the mechanical response by means of neutron diffraction and mechanical spectroscopy. At room temperature we observe a Fe$_3$Al-type ordered structure with a deficiency of Al in the 8c sites. The Ge atoms are distributed in the 4a and Al atoms in 8c sites. At high temperature we observe an order-disorder transformation when the crystal structure becomes Fe-α type. This loss of order gives rise to the hysteresis behavior of damping between the heating and cooling runs.

1. Introduction
The use of Fe-Al-Ge alloys in technological applications depends mainly on its brittle and creep behavior at high temperatures. It is of special interest to know the evolution of the structural phases with temperature in this ternary system, since it has a strong influence on dislocations and grain boundaries mobility [1, 2, 3]. The information about the structure of ternary Fe-Al-Ge system is very scarce, being it related to a partial isotherm [4], but the lack of data concerning its mechanical and magnetic properties is even deeper.

In this work, we combine neutron thermo-diffraction and mechanical spectroscopy (MS, damping and modulus measurements as a function of temperature), including amplitude-dependent damping analysis, in order to reveal the phase transitions and their effects on the mechanical properties of the Fe - 8at.%Al - 4at.%Ge alloy. The amplitude-dependent damping is a term that encompasses the damping processes in systems for which this damping is dependent on the deformation. In our analysis we study a magnitude (S) measuring the strength of these particular damping processes.

2. Experimental
We used polycrystalline samples of Fe - 8at.%Al - 4at.%Ge, which were homogenized at 1323 K during 1 h under high vacuum (10$^{-2}$ Pa), and then quenched in room-temperature water. Then, we cut the samples in small parallelepiped bars (around 0.3 × 0.3 × 1.5 mm$^3$) using a cooled kerosene low-speed saw. We give more details about the sample preparation elsewhere [5].
Figure 1. (Left panel) Theoretical (111) and (002) reflections of the ordered Fe$_{4-x}$Al$_x$ structure as a function of occupation factor of Al in the 8c sites. (Right panel) Measured patterns around 92° for Fe - 8at.%Al - 4at.%Ge alloy. At temperatures around 1000 K, the reflection (321) of the disordered Fe-α phase type is clearly distinguished.

We performed neutron powder thermo-diffraction (NPD) experiments at the high-flux D20 diffractometer [6] at the Institut Laue-Langevin, using high-intensity mode and a wavelength of 1.12 Å. We used vanadium cylinders as sample containers, which were placed in a standard vanadium furnace (a cylindrical heating element of 35 mm in diameter). This furnace was in turn located in a vacuum chamber (10$^{-2}$ Pa) and samples heated with a ramp of 3 K/min. During this heating process we registered a diffractogram every 5 min, then integrating 15 K. Thanks to the large banana-like detector, each diffractogram covers a scattering angle range of about 150°. We analyzed the diffraction patterns using standard software, such as FULLPROF [7] for Rietveld refinement and Topas® for texture effects with spherical harmonics approximation.

We performed MS measurements at frequencies close to 1 Hz, under high vacuum (about 10$^{-5}$ Pa), with free decaying vibrations during subsequent heating and cooling runs at 1 K/min [8, 9, 10, 11, 12]. We used samples with a parallelepiped shape (0.5 × 2 × 20 mm$^3$) and with a maximum strain of $\epsilon_0 = 5 \times 10^{-5}$. We fitted the area of free decaying vibrations in logarithmic scale with polynomials minimizing the $\chi^2$. The derivative of the decaying areas (in log scale) as a function of period number [8, 13, 14, 15] gives the damping $Q^{-1}$ as a function of $\epsilon_0$. We obtain the strength of the amplitude-dependent damping effects ($S$) as $S = \Delta Q^{-1}/\Delta \epsilon_0$, where $Q^{-1}$ is the damping change measured when the amplitude changes $\Delta \epsilon_0$. In fact, $S$ is an average slope value of $Q^{-1}$ against $\epsilon_0$ curves, in the whole strain interval; a positive value indicates that the greater is the deformation, the greater is the damping.

3. Results
Since the studied samples consist in a few small parallelepipeds, i.e., they are not isotropic powders, there exists a low number of domains satisfying the diffraction condition at each scattering angle. This has two consequences: (1) the presence of a strong texture effect, and (2) changes in the intensities of the diffracted peaks due to small sample movements associated with dilatations during heating. In order to reduce these effects we taken the average of eight consecutive patterns for each temperature range.

The Fig. 1 (left panel) shows simulated diffractograms for Fe$_{4-x}$Al$_x$ compounds (space group Fm$\overline{3}$m) with the aluminum atom at 8c sites. It is apparent that the intensities associated with the Bragg planes with high-Al content decrease with the Al occupation factor. If the occupation factor of Al is less than 20%, the (111) reflection almost disappears. Since the aluminum...
concentration in the sample is 8 at.%, it is impossible to detect an ordered structure from these reflections. Bearing this in mind, the presence of an ordered phase was detected by inspecting the peak splitting at high angles.

The Fig. 1 (right panel) shows the diffracted peaks at around 92° for temperatures between 300 K and 1200 K. The temperature associated to each diffractogram corresponds to the mean temperature of the interval in which the averages were performed. At high temperature we observe two reflections at around 92°, whereas at room temperature only one reflection (around 93.4°) appears. The presence of two peaks at high temperature is associated with the presence of two crystalline structures. As the temperature decreases, the peak associated with Fe-α decreases at the expenses of the other. In order to model this behavior, we tested different structures involving Fe, Al and Ge and describing the diffracted patterns. The best fitting model for data at room temperature is composed of a Fe₃Al-type structure with atoms at the positions and with the occupations shown in Table 1.

The Fig. 2 shows the final Rietveld refinements, where we observe that the strong texture effects could not be completely modeled with spherical harmonic functions (top panel), thus the fit goodness is quite poor (Rwp factor around 10%). Nevertheless, the lattice parameters of the Fe-α and Fe₃Al phases were accurately obtained, resulting in (2.923 ± 0.003) Å for Fe-α at
Table 1. Crystallographic data of the Fe₃Al-type structure ($Fm\bar{3}m$) used to model the diffractograms at 300 K.

| Element | Position | % Occ. factor |
|---------|----------|---------------|
| Fe      | $4a (0,0,0)$ | 86            |
| Ge      | $4a (0,0,0)$ | 14            |
| Fe      | $4b (1/2,1/2,1/2)$ | 100           |
| Fe      | $8c (1/4,1/4,1/4)$ | 97            |
| Al      | $8c (1/4,1/4,1/4)$ | 3             |

1200 K and $(5.752 \pm 0.002)$ Å for Fe₃Al at 300 K. The bottom panel shows the high-temperature diffractogram, where we observe a coexistence of the ordered (Fe₃Al type) and disordered (Fe-α type) phases, the latter being predominant [16].

Damping measurements exhibit a hysteresis behavior between the heating run performed up to temperatures over 950 K and the subsequent cooling, see the Fig. 3, which is in agreement with the order evolution shown above from NPD studies [8, 9, 10, 11, 12]. In fact, the decrease in the order degree above 950 K leads to an increase in the dislocation mobility giving rise to the recovery of quenched-in dislocations at elevated temperatures. Thus, during the cooling run, the height of grain boundaries peaks related to the solvent and solute [14, 15] increases due to
the reorganization of the structure [8, 9, 10, 11, 12]. In addition, the strength of amplitude-dependent damping (S) shows a change in slope at around the temperature where the order degree markedly decreases (see inset in Fig. 3) due to the increase in the dislocation mobility. The behavior of S as a function of temperature is also in agreement with the evolution of the order shown above and with previous works [8].

4. Conclusions
We determined the structure of Fe - 8at.%Al - 4at.%Ge using the neutron thermo-diffraction technique. At room temperature we found a Fe$_3$Al-type ordered structure with a deficiency of Al in the 8c sites. The Ge atoms are distributed in the 4a and Al atoms in 8c sites and we observe an order-disorder transformation at around 950 K when the crystal structure becomes an Fe-α type.

The disappearance of the order over 950 K gives rise to the hysteresis behavior of damping between the heating and the cooling runs, when the sample is heated over the phase transition temperature. The strength of the amplitude-dependent damping clearly reveals that at 950 K an order-decrease process is taking place.

Acknowledgements
The Institut Laue Langevin (ILL) is acknowledged for the allocated neutron beam time (Exp. 1-1-94), and D20 team for the help conducting the experiments. This work was partially supported by the CONICET, PIP 0179, and the PID-UNR; ING 290 and 453. The authors also want to thanks Prof Igor Golovin for supplying the samples.

References
[1] Bozorth R M, 1951 Ferromagnetism, MacMillan, London.
[2] Brandes E A, Brook G B, 1999 Smithells Metals Reference Book, Butterworth/Heinemann, Oxford.
[3] Cullity B D, 1972 Introduction to Magnetic Materials, Adison Wesley, Reading.
[4] Raghavan V, 2002 J. Phase Eq. 23, 437.
[5] Golovin I S, Strahl A, Neuhäuser H, 2006 Int. J. Mater. Res. 97, 1078.
[6] Hansen T C, Henry P F, Fischer H E, Torregrossa J, Convert P, 2008 Meas. Sci. Technol. 19, 034001.
[7] Rodríguez-Carvajal J, 1993, Physica B 192, 55.
[8] Lambri O A, Pérez-Landázabal J I, Gargicevich D, Recarte V, Bonifach F G, Cuello G J, Sánchez-Alarcos V, 2015, Mater. Trans. JIM 56, 182.
[9] Lambri O A, Pérez-Landázabal J I, Cano J A, Recarte V, 2004, Mater. Sci. Eng. A 370, 459.
[10] Lambri O A, Pérez-Landázabal J I, Cuello G J, Cano J A, Recarte V, Siemers C, Golovin I S, 2009, J. Alloys Compounds 468, 96.
[11] Lambri O A, Pérez-Landázabal J I, Recarte V, Cuello G J, Cano J A, Golovin I S, 2012, J. Alloys Compounds 537, 117.
[12] Lambri O A, Pérez-Landázabal J I, Cuello G J, Gargicevich D, Recarte V, Bonifach F G, Giordano E D, Sánchez-Alarcos V, 2014, Neutron News 25, 37.
[13] Lambri O A, 2000, in Materials Instabilities, ed. by J. Martínez-Mardones, D. Walgraef and C. H. Wörner, (World Scientific, New Jersey, 2000) pp. 249-280
[14] Schaller R, Fantozzi G, Gremand G (Eds.), 2001 Mechanical Spectroscopy $Q^{-1}$, Trans. Technical Publication, Uetikon-Zuerich Switzerland.
[15] Nowick A S, Berry B S, 1972 Anelastic Relaxation in Crystalline Solids, Academic Press New York
[16] Momma K, Izumi F, 2011, J. Appl. Crystallogr. 44, 1272.