ESRF	**Experiment title:** Atomic structure of Ca–based metallic glasses investigated by in situ high energy diffraction and ex situ absorption spectroscopy	**Experiment number**: MA-2498
Beamline: **ID22, ID26**	**Date of experiment**: from: 27 August 2015 to: 4 September 2015	**Date of report**: 23 November 2015
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Report: The goal of our experimental measurements at ESRF was a detail study of the atomic structure of various binary Ca–Al and ternary Ca–Al–X (X: Mg or Zn) and Ca–Mg–Zn metallic glasses by means of two investigation methods: a) in situ high energy X-ray diffraction – the glassy samples were studied at room temperature, upon heating/cooling cycles, in the process of crystallisation and in the molten state, b) ex situ X-ray absorption spectroscopy – the glassy samples were studied at various stages of their processing (in the as-prepared amorphous state, in the relaxed amorphous and in the pre-annealed crystalline state). Composition of the glasses was chosen according to their glass forming ability [1,2]. The obtained data provides a solid basis for structure modelling of the glasses.
Firstly, to get an initial image of the amorphous alloys' atomic structure, we performed on ID22 in situ high energy diffraction measurements (λ= 0.15489 Å, beam dimension 0.5×0.5 mm, transmission geometry) by using the Perkin Elmer XRD 1611 2D detector in asymmetric collection: we realised heating/cooling cycles with a ramp rate of 10 K min^{-1} (Cyberstar hot gas blower) between room temperature and the glass transition temperature (e.g. ~ 380 K for the Ca–Mg–Zn glasses). After the cycling we also measured the alloys during crystallisation and in the molten state (up to ~ 870 K). Prior to the measurements, the glassy samples were loaded into quartz glass capillaries under helium atmosphere. A typical result of the experiments are quality diffraction patterns (examples in Fig. 1), enabling a detailed revelation of the glasses' atomic structure. Diffraction patterns of the amorphous samples exhibit a pronounced and broad first peak followed by damping oscillations, which are visible up to ~ Q=15-18 Å^{-1} - these diffraction patterns are specifically suitable to

evaluate the glasses' atomic structure at room temperature and during the temperature cycling.

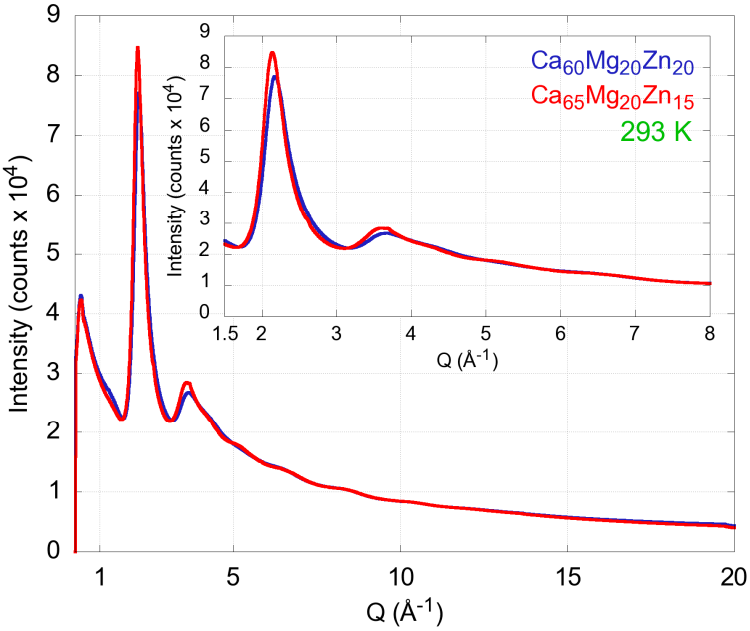

Fig. 1 Diffraction patterns of $Ca_{60}Mg_{20}Zn_{20}$ and $Ca_{65}Mg_{20}Zn_{15}$ metallic glass at 293 K in the Q region of ~0-20 Å^{-1}. The inset shows diffraction patterns in the Q region of 1.5-8 Å^{-1}.

The collected data clearly shows a significant dependence of the atomic structure of the alloys on their composition also within the Ca–Al, Ca–Al–X and Ca–Mg–Zn system. Because the atomic radius of Ca significantly differs from the atomic radius of other metals included in the alloys (i.e. Al and Zn), in the 1st coordination shell of the alloys' pair distribution function $G(r)$ one can clearly observe split peaks. According to our present analysis, in the case of e.g. Ca–Al glasses dominant are the Ca–Ca and Ca–Al atomic pairs, while for the Ca–Mg–Zn system dominant are the Ca–Ca and Ca–Zn atomic pairs.
Secondly, to get (more) complete image of the amorphous alloys atomic structure, we additionally performed on ID26 absorption spectroscopy measurements at room temperature (~ 30 minutes per decent spectrum). The XANES and EXAFS measurements were done at and above the Ca K-edge (4.038 keV) and the Zn K-edge (9.659 keV) in transmission and fluorescence mode. The samples were during the measurements mounted in a plastic frame. Hence, the absorption experiments allow us to evaluate location of the nearest atomic neighbours around the Ca and Zn atoms contained in the metallic glasses.
The obtained diffraction and absorption spectroscopy data enables modelling the metallic glasses' atomic structure by the Reverse Monte Carlo method. Moreover, an in-depth analysis of the data by the common neighbours analysis or the Voronoi tessellation methods will be done. We expect to publish results from these measurements in 2 or 3 scientific papers in high impact journals devoted to condensed matter physics and material science. All our expectations relating the experimental measurements have been fulfilled.

References

[1] F.Q. Guo, S.J. Poon, G.J. Shiflet, Appl. Phys. Lett. 84 (2004) 37-39.
[2] O.N. Senkov, J.M. Scott, J. Non-Cryst. Solids 351 (2005) 3087–3094.