	Experiment title: Structural relaxation and excess free volume in metallic glasses studied by in situ X-ray Diffraction	**Experiment number**: HC643
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Report:

Discovered in the 60s, metallic glasses (MGs) are relatively new materials characterized by a disordered structure which results in a macroscopic behavior that strongly differs from that of the polycrystalline state, and which leads to unique and excellent mechanical properties: a very high tensile strength, a high elasticity and a very good corrosion resistance. However, their wide usage is still limited by the metastable nature of the glassy state. The understanding of the glass formation and the relation between the structure, the atomic motion and the unique properties of these remarkable materials is therefore not only fundamental from a theoretical point of view, but it is clearly unavoidable if one wants to use them for practical applications.
Several works have shown the presence of internal stresses or frozen-in excess free volume in rapidly quenched metallic glasses, which lead to a more liquid-like elastic behavior of the material and lower elastic moduli. By combining *in situ* x-ray diffraction (XRD at ID15) and time resolved x-ray photon correlation spectroscopy (XPCS at ID10) measurements, we have been able to investigate the structural and dynamical changes occurring at the atomic length scale upon annealing of rapidly quenched Mg-based and Pd-based metallic glasses.
The XPCS data have been already measured by us in both systems by looking at the evolution of the dynamics for a wave vector q corresponding to the maximum of the first sharp diffraction peak (FSDP) of the static structure factor. As discussed in the proposal, we found a stress-dominated dynamics in the glassy state, characterized by a fast, exponential evolution of the structural relaxation time upon isothermal annealing in the deep glassy state. In order to link structural and dynamical changes we performed XRD measurements by

performing time-dependent studies at different annealing temperatures in the glassy state, and temperature cycling above and below the calorimetric glass transition temperature. In this way we can compare the data with both previous temperature dependence studies obtained in other MGs and with the atomic dynamics measured by XPCS.

Depending on the scattered intensity, several ribbons were used and kept in a resistively heated furnace, providing a temperature stability of 0.1 K. During all experiments, the temperature, T, was changed by keeping a fixed heating or cooling rate of 1 K/min.

In order to seize the subtle shape changes of the FSDP due to the release of internal stresses, we have fitted it choosing as fitting range the one where the intensity is larger than 30% of the maximum, and as modeling function an asymmetric pseudo-Voigt, to account for its asymmetric shape. In this function the full width half maximum (FWHM) changes with q as

$$FWHM = \frac{2\Gamma}{(1+e^{\eta(q-q_0)})} \qquad (2)$$

Figure 1 shows preliminary results on the evolution of the position of the maximum and the intensity of the FSDP during an isothermal annealing in the glassy state. Both quantities have been rescaled for their initial value. Assuming the atomic environments does not suffer important changes during the annealing, the position of the FSDP can be related to the relative volume change in the material as $V/V_0=(q_0/q)^3$.

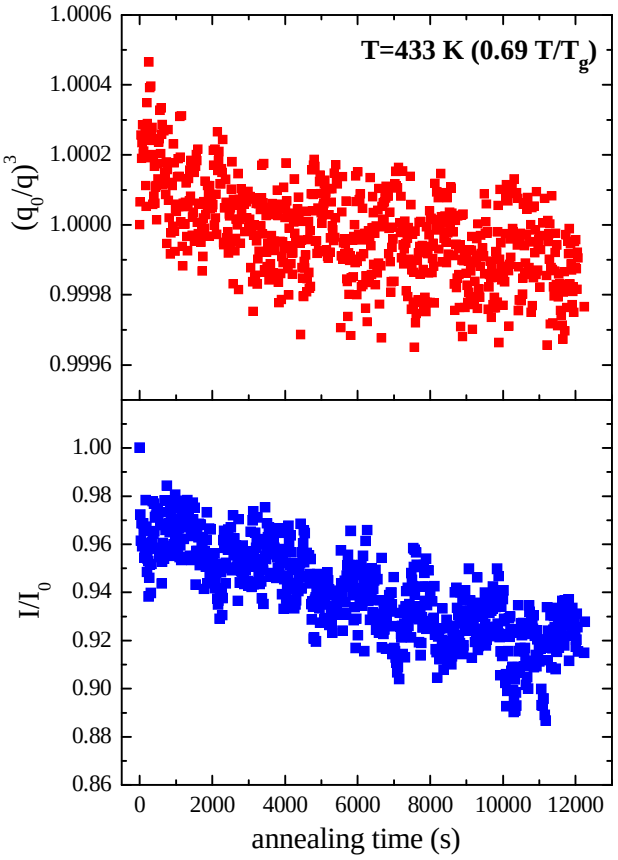

Figure 1: Evolution of the position and intensity of the FSDP during isothermal annealing in the glassy state.

We find that the glass structure is not stationary and subtly changes during the annealing, leading to an annihilation of the free volume or the internal stresses stored in the system during the quenching, and to therefore a more solid like-behavior of the glass. These results together with the exponential physical aging observed in the dynamical data support the idea of a stress-dominated dynamics in the glassy state and can be used to quatitive test the validity of different models of relaxation in glasses, like the free volume and the shoving model.

Interestingly, the small structural changes here observed reflect in a drammatically slow down of the atomic dynamics of more than one order of magnitude in the very same experimental conditions. This behavior is a consequence of the intrinsic kinetic nature of the glass transition.