

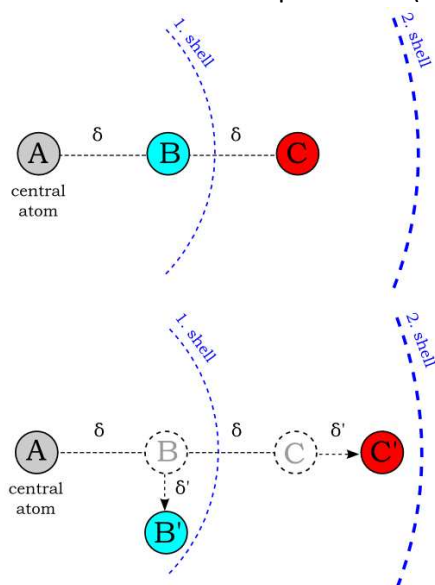
Extra Supplementary Information (ESI)

“In-situ XRD studies of nanocrystallization of Fe-based metallic glass:
 Comparative study by reciprocal and direct space methods”

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Experimental observations indicate that different coordination shells of a pair distribution function (PDF) exhibit different expansion rates. One could argue with such a claim by following “gedanken” experiment. Assume three atoms, ABC, to lie equidistant on a line at temperature T. Then we place an observer on atom A and start heating. If the expansion is higher at higher shells then distance between AB, $d(AB)$, is smaller than the distance between BC, $d(BC)$, i.e. $d(AB) < d(BC)$. However for an observer on atom B one will observe $d(BA) = d(BC)$ since they are in the same surrounding shell.

It should be noted here that suggested “gedanken” experiment strongly assumes one-dimensional (1D) atomic structure of the investigated material. However that is not true. The true structure is indeed three-dimensional (3D). Let’s just imagine a situation when atoms B and C in the previous example are moved by the same distance $\delta' = \delta/10$, but in different directions. We move atom C to position C' and atom B to position B' (see illustration below).



Relative length changes are then

$$1. \text{ shell, } \frac{|AB'| - |AB|}{|AB|} = \frac{\delta \sqrt{\frac{101}{100}} - \delta}{\delta} \cong 0.005$$

$$2. \text{ shell, } \frac{|AC'| - |AC|}{|AC|} = \frac{2\delta + \frac{\delta}{10} - 2\delta}{2\delta} = 0.050$$

This simple example suggests that the relative length change in the second shell is larger than in the first shell. This is in agreement with our observations.

The problem with usual XRD experiment is that one is collecting an angular distribution of intensities and the phase of the diffracted photons is lost. When collecting diffracted photons with a two-dimensional (2D) detector one gets a projection of the three-dimensional (3D) structure. Here we lose one dimension. In case of our

studies we found that the studied sample does not show any preferential orientation (it is indeed isotropic). Therefore the obtained 2D XRD patterns could be radially integrated. This procedure yields a one-dimensional intensity distribution. In other words we analyzed the diffracted data with respect to the magnitude of the wave momentum vector transfer $|Q| = 4\pi \sin(\theta)/\lambda$. From the measured intensities $I(Q)$ we derived corresponding structure factors $S(Q)$. The sine Fourier transform of the structure factor $S(Q)$ represents the reduced pair distribution function $G(r)$

$$G(r) = 4\pi r [\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^\infty Q [S(Q) - 1] \sin(Qr) dQ.$$

$G(r)$ actually describes how the local atomic density $\rho(r)$ varies with respect to the mean atomic density ρ_0 as a function of the radial distance r from any arbitrary atom in the sample. Despite the fact that the structure factor $S(Q)$ and the reduced pair distribution function $G(r)$ are one-dimensional functions, they represent projections from the 3D atomic structure. In other words, structural changes always occur in 3D but we detect them only from a 1D projection. Therefore it is not appropriate to explain rather complicated structural changes occurring in 3D by proposing a naïve 1D structural model. Our simple 2D model contradicts proposed the 1D model and shows agreement with our experimental observations.