

Nanostructure of Amorphous Materials Using Electron Cross-Correlation Analysis

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The microscopic knowledge of structures of materials is mainly based on information gained from the diffraction of photons, electrons or neutrons. These techniques allow the determination of the structure of most, even complex, crystalline materials. Also defects in crystalline material can be analyzed with high precision. Advanced HRTEM allows the determination of the positions of atom columns with pm accuracy. In contrast, for disordered matter the only accessible structural information (by standard diffraction) is the distribution function of distances between pairs of atoms, the so-called pair distribution function [1]. The reason for the missing bond angle information is the implicit ensemble and time average, which is involved in diffraction, based on a chaotic source.

Ensemble averaging can be avoided if the coherence volume of a partially coherent electron beam (or X-ray beam) is equal to the illuminated sample volume. In this case all photons scatter in phase.

By forming higher order correlation functions it is possible to access and classify the otherwise hidden local bond-orientational order as well as the medium-range order (MRO) in disordered matter. Bond-angle information requires the correlation of at least three different “molecules” in the sample.

Fluctuation electron microscopy (FEM) as well as X-ray cross correlation analysis (XCCA) investigate the higher order correlations. FEM is most suited to study the MRO in glasses [2, 3]. Recently, XCCA experiments evidenced the existence of icosahedral symmetries in colloidal glasses [4]. In this paper the concept of XCCA will be applied to FEM. This should allow the testing of local symmetries, e.g., in metallic glasses.-

The mechanical properties of metallic glasses (MG) are largely dependent on their nanoscale structural ordering. Many studies have been completed on the short-range order of metallic glasses, indicating a preference for icosahedral-type short-range order. However, the prevalent nanostructure present at medium range length scales in most metallic glasses remains a debate. Cu-Zr binary metallic glasses are good glass formers over a large composition range and serve as a useful model system to study medium-range structural order in metallic glasses. The Cu-Zr MGs are predicted to be comprised of networks of icosahedra, with the highest concentration of interconnected icosahedra occurring at Cu₆₅Zr₃₅ [5]. However, other studies have shown evidence of planar-type ordering [2] related to the FCC structure of copper.

Here results will be reported on structural order present in Cu_xZr_{1-x} via analysis of the angular cross-correlations in nanobeam electron diffraction. Wochner, et al. [4], have recently demonstrated this approach using coherent x-ray nanodiffraction patterns from colloidal glasses as a method to identify local symmetries [3]. By applying the cross-correlation analysis (CCA) technique to the collected nanobeam electron diffraction patterns, we can study the compositional dependence of the structural order in Cu-Zr MGs.

For our experiments, amorphous ribbons of Cu_xZr_{1-x}, (Cu composition varying from x = 0.45 to 0.645), were synthesized using a melt-spinning technique. Samples are electropolished to a thickness of ~ 25 nm for the scanning transmission electron microscope (STEM). Spatially coherent electron probes of FWHM 1-3 nm in size, R, were formed in nanodiffraction mode in the STEM, using a 5 μm condenser aperture. A series of 200 or more nanodiffraction patterns were collected and analyzed for each composition. The normalized 4-point cross-correlation function C_k(Δ) was then calculated for each nanodiffraction pattern, defined here as,

$$C_k(\Delta) = \frac{\langle I(R, r_p, k, \phi) I(R, r_p, k, \phi + \Delta) \rangle_\phi}{\langle \langle I(R, r_p, k, \phi) I(R, r_p, k, \phi + \Delta) \rangle_\phi \rangle_\Delta} - 1$$

where ϕ is the azimuthal angle, k is the reciprocal lattice vector, Δ defines the angular separation along the intensity ring and r_p its position. The cross-correlation function is directly related to bond-orientational order in the system. The periodicity or symmetry of the cross-correlation function can then be extracted via Fourier transform. The amplitude C_k^l of the l th Fourier component of $C_k(\Delta)$ affords the contribution of l -fold symmetry at each k value. Figure 1 shows the average Fourier components of $C_k(\Delta)$ for $\text{Cu}_{64.5}\text{Zr}_{35.5}$. The ensemble average of C_k^l is needed to describe the general structural order in the system. The average C_k^l reveals local symmetries at distinct values of k , whereas the azimuthally averaged diffraction intensity for $\text{Cu}_{64.5}\text{Zr}_{35.5}$ shows no indication of structural ordering, besides the well-known pair-correlations. From the experimental data, we are able to extract the compositional dependence of the local symmetries, coupled to particular values of k . To link the extracted symmetries to higher order correlations and atomic structure, the acquired nanodiffraction patterns are used to retrieve model-free potential functions in the framework of the reciprocal-space configurational approach for inhomogeneous systems, based on the correlation correction algorithm [7] and atomic density function theory [8]. This, in turn allows us to calculate all desired statistical properties of the disordered system. Future work that includes a larger compositional range will allow us to better understand the variation in local symmetries present in the Cu-Zr system.

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Fig 1. Average C_k^l for $\text{Cu}_{64.5}\text{Zr}_{35.5}$, computed from 200 nanodiffraction patterns.

