

## “Crystallography” of an Amorphous Material Using Electron Nanodiffraction

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Most electron microscopists have seen the characteristic fuzzy rings of large-area diffraction from an amorphous material at one time or another, if only as a result of a failure of sample preparation for a crystalline sample. This kind of scattering can be normalized and Fourier inverted to yield a pair distribution function,  $g(r)$ , that measures the mean number of atoms that sit a distance  $r$  away from the average atom in the material.  $g(r)$  is foundational data for studying the structure of amorphous materials, but it is not reminiscent of the symmetry-based analyses that form the basis of crystallography.

If the same amorphous material is studied with a coherent, nanometer-size probe beam of electrons, the fuzzy rings break up in small, bright speckles, as shown in Fig. 1e, which was acquired from a  $Zr_{65}Cu_{27.5}Al_{7.5}$  metallic glass thin film. Those speckles arise from Bragg diffraction from more-ordered local arrangements in the glass. As the probe is scanned from place to place, the speckles change in position and intensity because the probe illuminates different ordered regions. Fluctuation electron microscopy (FEM) is the study of the normalized variance  $V(k)$  of many speckles from many positions. FEM data derived from many patterns like Fig. 1e acquired from different positions is shown in Fig. 1a for films with varying deposition rate.

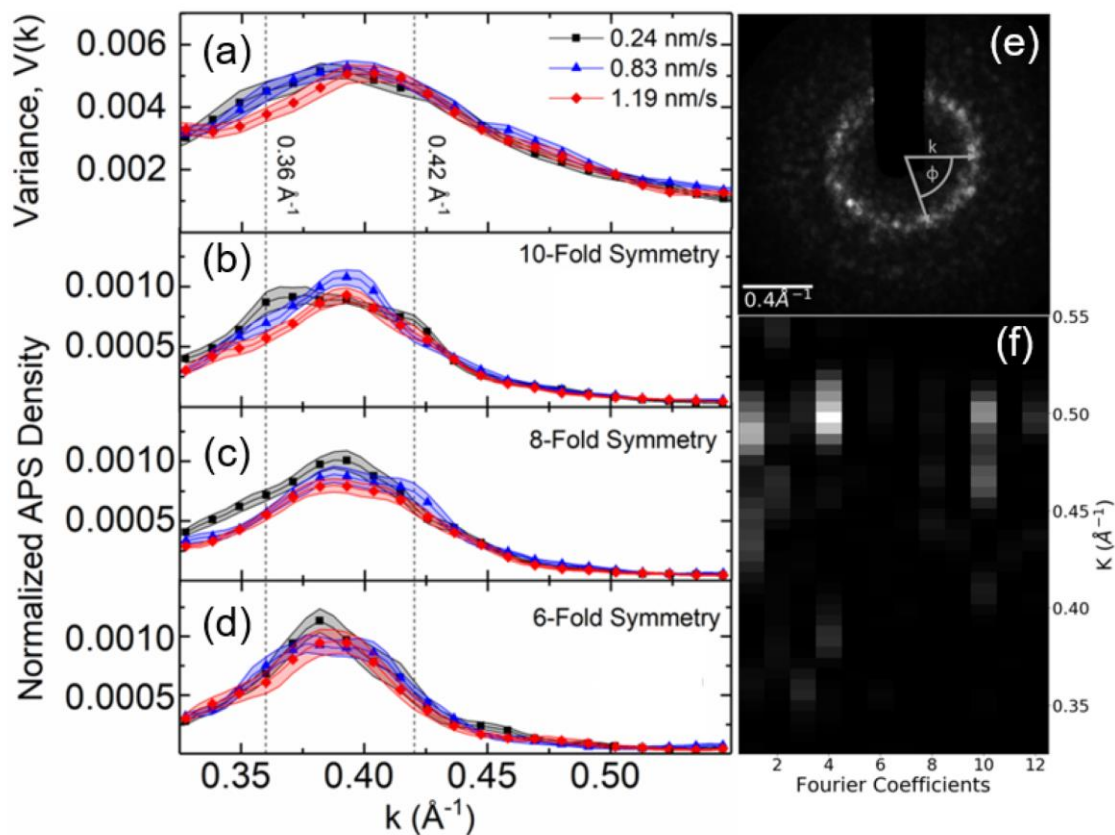
Based on extensive atomistic modeling, we have identified different peaks in  $V(k)$  of Zr-Cu-Al metallic glasses as arising from different structure types<sup>[1,2]</sup>. We attribute the low- $k$  shoulder near  $0.36 \text{ \AA}^{-1}$  to icosahedral local order, and the main peak at  $k$  near  $0.40 \text{ \AA}^{-1}$  and the shoulder near  $0.42 \text{ \AA}^{-1}$  to crystal-like order. Thus, the lower deposition rate films have increased icosahedral order compared to the highest rate sample.

In the atomistic models, the ordered structures are identified primarily by their approximate rotational symmetries, with icosahedra exhibiting only five-symmetries and crystal-like structures exhibiting four- and six-fold symmetries. Rotational symmetries in atomic arrangements should be reflected in rotational symmetry in diffraction. Various attempts to analyze rotational symmetries in electron nanodiffraction from amorphous materials have been made,<sup>[3,4]</sup> but they have been criticized for unphysical, odd-numbered rotational symmetries.<sup>[4]</sup> Fig. 1f shows the angular power spectrum (around  $f$  in Fig. 1e) for the pattern shown in 1e. While the even numbered symmetries are systematically stronger, the odd numbered symmetries are non-zero. Recently, Im *et al.* showed conclusively that odd-ordered symmetries are a sample thickness effect,<sup>[5]</sup> probably arising from random correlations between diffraction from different ordered regions through the thickness of the sample. For thin enough samples, the even-ordered symmetries reflect the real structure of the material.

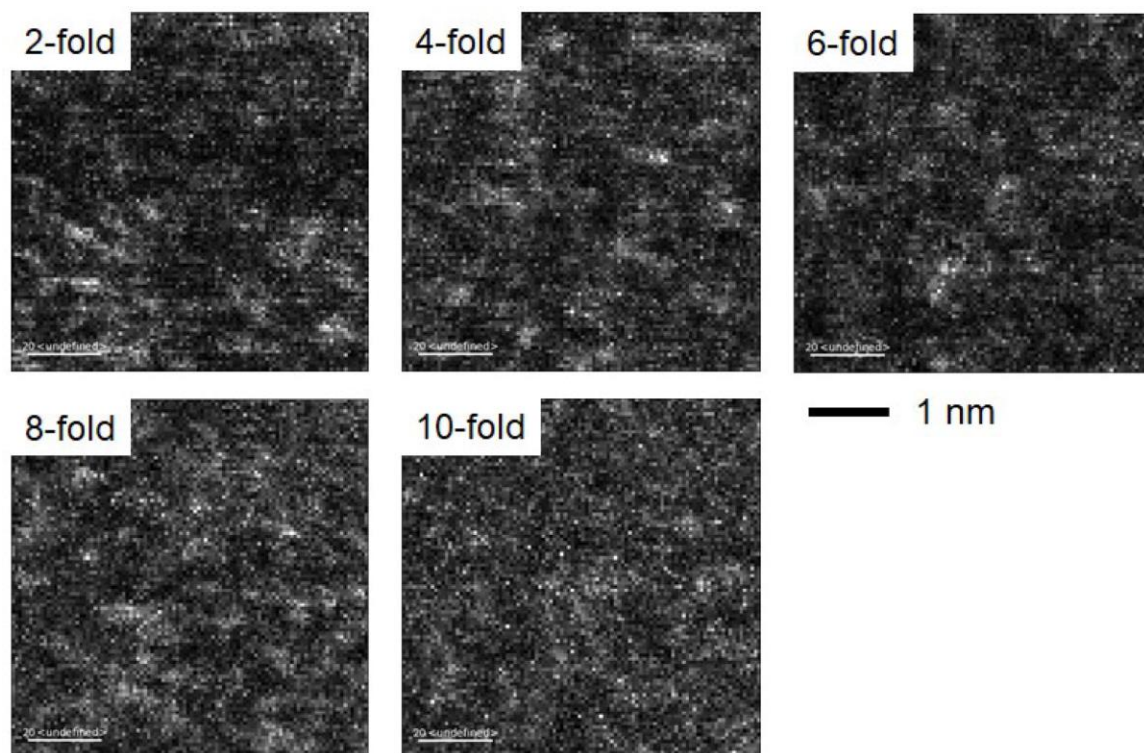
The films used for Fig. 1 are thin enough to minimize odd-symmetry artifacts, so Fig. 1(b)-(d) show the angular power spectrum as a function of  $k$  for 10-, 8-, and 6-fold symmetries averaged over all the data used to create Fig. 1a. The 10-fold symmetry has a distinct peak at  $k = 0.36 \text{ \AA}^{-1}$  for the lowest deposition rate, confirming the identification of this peak in  $V(k)$  based on modeling from direct observation of approximate symmetry in diffraction. The six-fold symmetry is highest in the main peak, the 8-fold peak is highest at the  $k = 0.42 \text{ \AA}^{-1}$  shoulder, confirming the assignment of those peak to crystal-like order.

Rotational symmetry analysis therefore forms a sort of “crystallography” for local ordered structures in amorphous materials, in the sense that it allows us to identify rotational symmetries of those ordered regions. The next step is to use high-speed direct electron cameras to obtain quantitative measures of the size and number density of ordered regions. Fig 2 shows an example of this kind of data, acquired for a  $\text{Pd}_{42.5}\text{Ni}_{42.5}\text{P}_{15}$  metallic glass.<sup>[6]</sup> This glass does not have the strong 10-fold symmetry characteristic of icosahedral order, but it has similar strong 6-fold symmetry.

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**Figure 1.** Fig 1: Electron nanodiffraction from  $\text{Zr}_{65}\text{Cu}_{27.5}\text{Al}_{7.5}$  thin films as a function of deposition rate. (a) FEM data; (b)-(d) the average angular power spectrum of all the nanodiffraction patterns for the indicated rotational symmetry; (e) an example nanodiffraction pattern; (f) the power spectrum of the pattern in (e).



**Figure 2.** Fig. 2: Angular power spectrum maps for the indicated symmetry from a Pd<sub>42.5</sub>Ni<sub>42.5</sub>P<sub>15</sub> metallic glass acquired on a high-speed direct electron detection camera. The sample does not have strong 10-fold symmetry indicating little icosahedral order, but it does have strong 6-fold symmetry.

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