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# Quantitative measurement of density in a shear band of metallic glass monitored along its propagation direction

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## Abstract

Quantitative density measurements from electron scattering show that shear bands in deformed  $\text{Al}_{88}\text{Y}_7\text{Fe}_5$  metallic glass exhibit alternating high and low density regions, ranging from -9 % to +6 % relative to the un-deformed matrix. Small deflections of the shear band from the main propagation direction coincide with switches in density from higher to lower than the matrix and vice versa, indicating that faster and slower motion (stick-slip) occurs during the propagation. Nano-beam diffraction analyses provides clear evidence that the density changes are accompanied by structural changes suggesting that shear alters the packing of tightly-bound short- or medium-range atomic clusters. This bears a striking resemblance to the packing behavior in granular shear bands formed upon deformation of granular media.

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Metallic glasses (MGs) offer unique properties such as high strength, extended elasticity, high wear and corrosion resistance, or excellent soft magnetic behavior [1]. However, the limited ductility and especially the immediate catastrophic failure in tension once the elastic limit is reached are major obstacles to applications as structural materials [1]. This behavior has led to substantial effort towards understanding and improving the accommodation of plastic deformation in MGs, including the design of composites consisting of ductile crystalline phases in a bulk MG matrix [2–6]. Monolithic glasses with higher Poisson’s ratios near the ideal value of 0.5 [7–9] tend to have improved compressive and bending plasticity, and are reported to show a fine dispersion of shear bands [10]. Well below the glass transition temperature, plastic flow in metallic glasses is restricted to narrow regions called shear bands [11–13], widely believed to be dilated zones of increased free volume caused by shear localization enabling shear softening [14–16]. Thus, the density or free volume inside shear bands is often treated as key to understanding plasticity in MGs. Quite a large range of density or free volume changes have been observed, based on various experiments [15–23]. However, most experimental methods, including positron annihilation spectroscopy and calorimetry, measure the free volume integrated over the entire sample to be typically from +1 % to +3 %. High resolution transmission electron microscopy has shown the presence of nanovoids inside shear bands, believed to form from the coalescence of atomic-sized free volumes after deformation [24], but so far has not been used to measure material density either on average or locally within the shear band.

**Previously the local density within shear bands in  $\text{Al}_{88}\text{Y}_7\text{Fe}_5$  has been probed at selected positions and for different shear bands using quantitative HAADF-STEM on deformed and un-deformed metallic glass regions (see Supplementary Material [25] for details). These experiments showed both positive and negative density changes for shear bands with respect to the un-deformed glass [26]. Minor compositional changes relative to the matrix were observed in the shear band segments. While compositional changes contributed mainly to the positive density variations in the bright shear band segments, the change in free volume was the dominant effect for the dark shear band segments.**

Here we show, by combining several quantitative electron scattering signals, that shear bands in  $\text{Al}_{88}\text{Y}_7\text{Fe}_5$  metallic glass have segments of both decreased and increased density that alternate along the propagation direction. The changes

in density are correlated to small deflections in the propagation direction and changes in medium-range structural order and chemical composition. Similar behavior has been reported for granular media, but not for amorphous solids. One important implication is that individual shear bands apparently propagate via local, segment-wise stick-slip that might originate from their complex topology. These results are important to the physics of deformation in metallic glasses, and suggest connections to the physics of granular materials and jammed systems.

Ingots of the target composition  $\text{Al}_{88}\text{Y}_7\text{Fe}_5$  were prepared by arc melting pure Al (99.999 %), Fe (99.99 %) and Y (99.9 %). Fully amorphous ribbons with a thickness of about 40  $\mu\text{m}$  were produced by melt spinning using a tangential wheel (Cu) speed of 47  $\text{ms}^{-1}$ . The melt-spun ribbons were cold-rolled to a thickness reduction of 23 % and subsequently prepared for transmission electron microscopy (TEM) by twinjet electro-polishing using  $\text{HNO}_3:\text{CH}_3\text{OH}$  in a ratio 1:2 at 253 K. The TEM study was performed with a FEI Titan 80-300 (probe) aberration-corrected transmission electron microscope operated at 300 kV in scanning transmission electron microscopy (STEM) mode. The following conditions were used during the experiments: a probe current of 15 pA, a collection semi-angle of 51.3 mrad for the high-angle annular dark-field (HAADF) detector (130 mm camera length), a convergence semi-angle  $\alpha$  of 0.6 mrad, a nominal spot size of 2 nm and a step size of 2 nm. For electron energy loss spectroscopy (EELS) we used a collection semi-angle  $\beta$  of 5.73 mrad, an entrance aperture of 2.5 mm, an energy dispersion of 0.1 eV/channel and an acquisition time of 0.02 s. The fluctuation electron microscopy (FEM) data were obtained from energy-filtered nanobeam diffraction using a camera length of 510 mm.

HAADF-STEM images from deformed  $\text{Al}_{88}\text{Y}_7\text{Fe}_5$  such as Fig. 1 frequently showed shear bands with contrast changes from bright to dark and vice versa along their propagation direction. Each contrast reversal is accompanied by a slight deflection [26], always within  $\pm 5^\circ$  of the main propagation direction of the shear band. The propagation direction is determined from the bifurcation. The angular deflection range matches the angle between the shear bands and the direction of the applied shear stress reported in literature [13]. However, we do not suggest that the density changes in the shear bands, which are introduced hereafter, caused the deflections but rather that they seem to be inherently connected with the local topology of shear bands. Since glasses do not have a defined slip plane it is

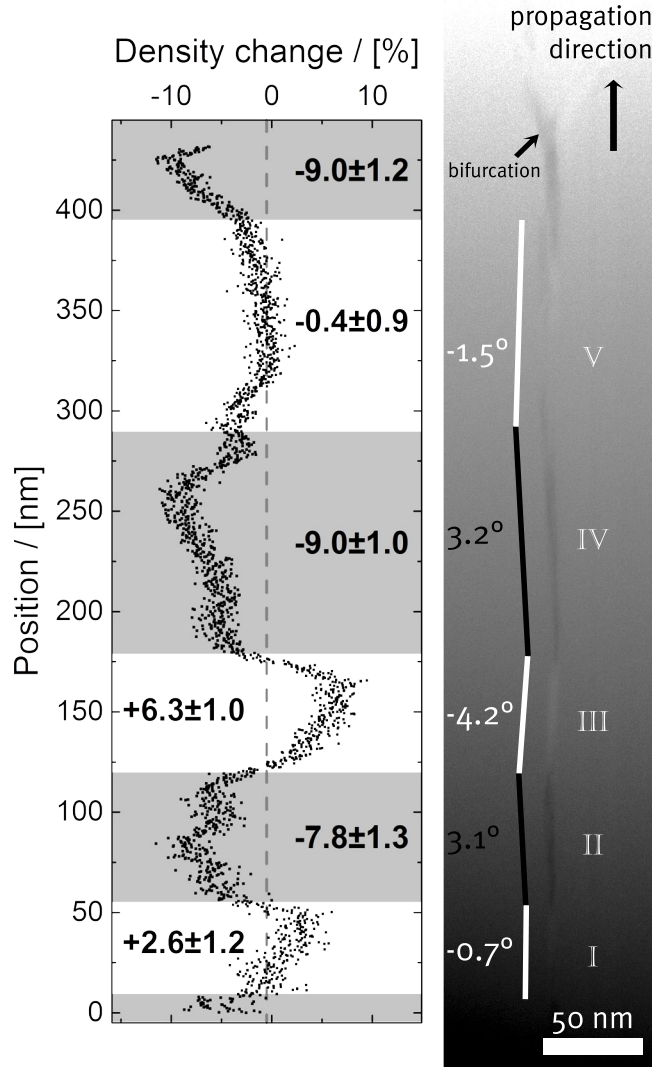


FIG. 1. **Density variations in a shear band.** Right: A HAADF-STEM image showing a shear band in cold-rolled  $\text{Al}_{88}\text{Y}_7\text{Fe}_5$  propagating from bottom to top with several contrast changes. The individual segments are numbered (I-V). The deflection angles are indicated for the segments. Left: Quantified density variations of the shear band along the propagating direction with respect to the un-deformed matrix. Bright and dark parts of the shear band are indicated by the white and grey background, respectively.

expected that shear bands have a non-planar topology with 'hills and valleys' along their propagation direction. This is also seen on larger length scales, when scanning electron microscopy images of shear bands are observed that do not follow a straight line, but vary slightly concerning their direction. Such a local topology leads, in an edge-on view, to locally different deflections from the main propagation direction. Also, once the shear band

has formed and slip continues along such a 'rough' band, the local topological characteristics may serve to hinder ('hills' or facilitate 'valleys') continued slip, giving rise to local variations of compressive and tensile stresses within the shear bands. Such topological features may also affect the local slip velocity along the given shear band.

Fig. 2 shows the foil thickness profiles from part of the sample area shown in Fig. 1 determined from low-loss EELS. There is a linear increase in foil thickness along the propagation direction of the shear band which is related to the wedge shape of the TEM specimen. There is also a slight thickness variation between the two sides of the shear band, probably due to the shear offset. Thickness profiles across the shear band show that there is no preferential thinning of the shear band by TEM sample preparation.

The density variation  $\Delta\rho$  of each bright or dark segment was determined from the HAADF intensity and EELS thickness, as described in detail in the **Supplementary Material [25]**. The left side of Fig. 1 shows the local density inside the shear band along its propagation direction. Repetitive density changes are observed. The density differences between shear band and un-deformed matrix range from  $(-9.0 \pm 1.0) \%$  to  $(+6.3 \pm 1.0) \%$ . The matrix region outside the shear bands does not show any impact of the deformation or of pre-existing density fluctuations. The integrated density change along this specific shear band is  $\Delta\rho = (-2.9 \pm 4.3) \%$ . No characteristic segment length was found over examination of many shear bands. However, the dark low density segments dominate the shear bands in general, which results in a negative value for the integrated density change. The mean density is in good agreement with previous reports of shear band density from macroscopic experiments [15, 22, 23]. The width of the shear band was measured on the clearest segments (II, III and IV) by fitting Gaussian peaks to the data in Fig. 1. The FWHM of  $w_{II} = (3.72 \pm 0.21) \text{ nm}$ ,  $w_{III} = (4.26 \pm 0.16) \text{ nm}$  and  $w_{IV} = (4.24 \pm 0.15) \text{ nm}$ . Segment V is wider by inspection, so the consistency of the width in the other segments shows that they image the shear band near edge-on. When the shear band is inclined, the projected density difference along the electron beam direction is suppressed due to the overlap of shear band and matrix.

At this point it might be appropriate to question whether the shear band structures analyzed resemble the structures formed during the shear band propagation. Since no crystal formation was found for the denser regions of the shear band, where crystallization may be

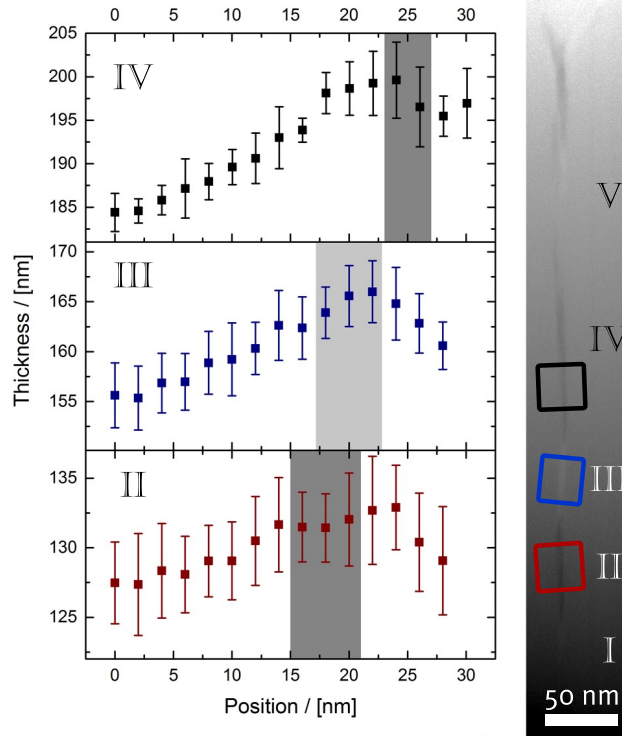


FIG. 2. **Foil thickness calculations.** Profiles of the averaged foil thicknesses for the boxed regions of the HAADF-STEM image displaying different shear band parts (see segments II, III and IV in Fig. 1). The grey shaded areas indicate the position of the shear band.

expected to be facilitated [27], it seems safe to assume that the shear bands analyzed in this work do closely resemble the structures present during deformation.

FEM provides information about the nanoscale order of the metallic glass from systematic coherent electron nanodiffraction (see **Supplementary Material**, Fluctuation Electron Microscopy) [25, 28, 29]. Nanoscale order leads to variability in nanodiffraction into different directions in reciprocal space, which is captured quantitatively in the annular mean of the variance image  $\Omega_{VImage}(k)$  [28]. Fig. 3 shows FEM data from a bright high-density segment (segment I), a dark low-density shear band segment (segment II) and the un-deformed matrix about 20 nm away from the dark shear band segment. The results for the lower density, dark segment are similar to our previous report [26], but we have obtained better statistical quality data for the higher density, bright segment here. After accounting for differences in sample thickness, the variance signal for the matrix is consistent with previous FEM studies of the same glass composition [29], which data showed that un-deformed

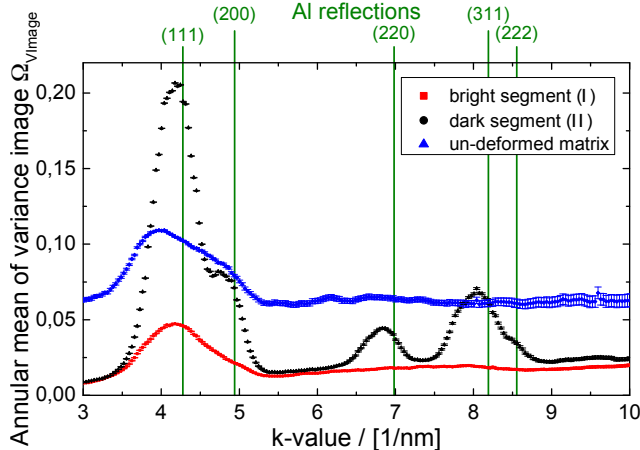


FIG. 3. **Fluctuation Electron Microscopy (FEM)**. Annular mean of variance image  $\Omega_{VImage}$  of different NBDP ensembles (un-deformed matrix, bright/dark parts of the shear band corresponding to the segments I and II).

$\text{Al}_{88}\text{Y}_7\text{Fe}_5$  contains nanoscale ordered regions with an internal structure similar to FCC Al embedded in a more disordered matrix. The primary peak in  $\Omega_{VImage}(k)$  sits near the Al  $\{111\}$  reflection, there is a shoulder at higher  $k$  consistent with Al  $\{200\}$ , and there are no peaks at higher  $k$ .  $\Omega_{VImage}(k)$  for the bright, higher density shear band segment is similar to the matrix, but the  $\{200\}$  shoulder is suppressed. This indicates a similar structure of Al-like regions embedded in a matrix, but with reduced size or internal structural order for the Al-like regions [26, 29].  $\Omega_{VImage}(k)$  for the dark, low density shear band segment indicates strikingly high structural order. In addition to clear  $\{111\}$  and  $\{200\}$  peaks, there are peaks at the  $\{311\}$  and  $\{220\}$  Al reflections as well [26]. However, all peaks are shifted towards lower  $k$  values. The reason for this has been shown to be hydrostatic tensile strain originating from the surrounding amorphous material in which the Al-like regions or clusters are embedded [29]. The increase in  $\Omega_{VImage}(k)$  shows that the Al-like regions are larger than in the matrix, and the persistence of peaks to high  $k$  shows that they have a higher degree of crystalline structural order [29]. Strong Al-like order is consistent with previous observations of Al crystallite nucleation in shear bands [27]. Here we emphasize that we have a mixture composed of Al-rich cluster/crystallites embedded in amorphous material present in the dark shear band segments rather than fully crystallized regions since the latter would produce enormous peaks in the fluctuation signal which we do not observe. Moreover, a former study showed that fully crystallized  $\text{Al}_{88}\text{Y}_7\text{Fe}_5$  metallic glass is composed of



three crystalline phases; that is, FCC Al, Al<sub>3</sub>Y (D0<sub>19</sub> structure) and a ternary intermetallic Al<sub>7</sub>Fe<sub>5</sub>Y phase [30]. Since the diffraction peaks of the FEM study closely match FCC Al with the other two crystalline phases missing, a complete crystallization of the dark shear band segment can be excluded here. We estimate the size of the ordered Al-like regions to be  $\leq 2$  nm from the similarity of adjacent nanodiffraction patterns [31]. Since we used a 2 nm diameter probe for the experiments, 2 nm is an upper bound and the real ordered regions may be even smaller. Moreover, for 3d transition metals such sizes are commonly associated with clusters rather than with the crystalline state.

Larger density decreases of 9 % or more as reported here must be accommodated by some local chemical changes, not just an increase in mean atomic spacing. A qualitative chemical analysis based on the Al-L edge showed an increase in the Al signal for the dark shear band segments and a decrease for the bright ones (Fig. 4d, **Supplementary Material [25]**) which is consistent with our previous report [26]. It is worth noting that the chemical changes observed are minor. They are typically balanced between Al and Fe. It was further shown that the Al enrichment and the corresponding Fe depletion were not sufficient to account for the total density change in the dark shear band segments. The dominating effect causing the density change was the variation in free volume. Based on the fact that Fe is not soluble in FCC Al, we can estimate the maximum density variation arising from compositional changes. If we replace all of the present Fe (5 at%) by Al, it would account for a maximum density decrease of roughly 4.5 % which is not enough to explain a density decrease of 9 %. Thus, the density drop for the dark shear band segments must include changes in free volume in addition to the changes in composition [26]. Further information can be obtained from the Zero Loss and Plasmon signal extracted from the EELS data. The increased Zero Loss signal (Fig. 4b) for the dark shear band regions indicates less scattering events due to less dense material at a constant foil thickness. On the other hand, the Plasmon peak (Fig. 4c) reveals an increase for such dark shear band segments, which also indicates that compositional changes (Al enrichment) must have occurred, since an Al increase enhances the free-electron density and thus the Plasmon signal.

The observation of an increased EELS ZLP for the dark shear band regions (see **Supplementary Material [25]** Fig. 4a) and enhanced diffusion along shear bands by more than six to eight orders of magnitude compared to diffusion in the un-deformed matrix [32] are perfectly consistent with enhanced free volume in the shear bands.

Structural changes inside shear bands have been analyzed indirectly by low-temperature heat capacity measurements on severely deformed metallic glasses [33, 34]. The so-called Boson peak revealed that the atomic structure was only modified inside the shear bands. Additional studies of the aging dependence of the Boson peak indicated that two different regions exist in the deformed specimens. One of these regions contributes to an accelerated aging of states since after identical relaxation treatment between room temperature and the glass transition, a state with lower enthalpy was attained by the deformed glass as compared to material without shear bands. Accelerated aging would be expected for the low-density regions of the shear band.

The HAADF image intensity shows no evidence for the formation of voids, but at this sample thickness it is insensitive to the small (1 nm diameter) voids previously reported [24]. Reasons for void formation are the presence of multiple deflections of the shear bands, stress concentrators and low-viscosity regions. Nanovoids would also explain the early and catastrophic failure as well as the observation of vein patterns [8, 13] at the fracture surfaces of metallic glasses.

The repeated switching between higher and lower density observed along the shear band is directly analogous to the deformation behavior of granular media. Fazekas *et al.* [35] have shown by simulations that deformation of idealized granular media composed of spheres led to the formation of shear bands with high and low density regions. They further showed that the critical density of the shear bands depends on friction which, in turn, defines a specific packing state. Thus the theoretical findings for granular media explain our observation of higher and lower density shear band regions as the result of friction causing faster and slower motion of the shear bands. However, in the absence of granules, what plays their role in the metallic glass? It could be atoms, but the persistence of a similar structure of Al-like regions in a more disordered matrix within both the dark and bright segments leads us to suggest that ‘the granules’ may instead be tightly-bound short- or medium-range atomic clusters, which can fill the space more or less efficient [36–38]. Shear alters the packing of those clusters, but does not strongly modify their internal structure.

In summary, we have quantified the density inside a shear band of deformed  $\text{Al}_{88}\text{Y}_7\text{Fe}_5$  metallic glass along its propagation direction. The local density varies enormously, ranging from -9 % to +6 %, compared to the un-deformed matrix. Slight deflections from the main propagation direction of the shear band are found to coincide with the density switching

from positive to negative values. The density alterations are attributed to compositional and free volume changes reflecting a different dense packing of atomic clusters, probably caused by different propagation speeds. These findings bear a striking resemblance to granular shear bands formed upon deformation of granular media [35].

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