Consequences of randomness: compositional contours in amorphous alloys

R. Gemma,† M. to Baben,‡,§ A. Pundt,¶ V. Kapaklis,‡ and B. Hjörvarsson‡,†

1Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Saudi Arabia
2Department of Physics and Astronomy, Uppsala University, Box 516, 751 20 Uppsala, Sweden
3Materials Chemistry, RWTH Aachen University, Kopernikusstr. 10, 52074 Aachen, Germany
4Institute of Applied Materials (IAM-WK), Karlsruhe Institute of Technology KIT, 76131 Karlsruhe, Germany

The physical properties of amorphous materials are only partially explored and the relation between local atomic arrangements and emergent physical properties are not fully understood. Crystalline materials are readily characterised with respect to structure and chemical composition using standard scattering techniques, while amorphous materials being disordered, do not offer that possibility. Since the pioneering work on the amorphization of metals and alloys, a large variety of methods are now available for their fabrication. While the end products are not always identical with respect to physical and chemical properties, it is challenging to identify the underlying reason for the observed differences. The atomic arrangements in amorphous alloys are not well-defined, exhibiting close resemblance to liquid like structures, rendering the task of linking their structure to the observed physical properties challenging. Here, we utilize one of the best studied amorphous magnetic alloys, Fe$_{1-x}$Zr$_x$, to address the relation between the distribution of the elements and the observed magnetic properties, using Atomic Probe Tomography (APT). We generalise our findings and contribute thereby to the formation of a conceptual base for the understanding of the physical properties of amorphous alloys.

Amorphous materials are known to exhibit extraordinary mechanical properties in which computational analysis demonstrate the existence of shear-resistant structural features, tightly linked to the presence of short-range order. High-density icosahedral packing of atoms, with a Voronoi coordination polyhedron with index $(0,0,12,0)$, i.e. all nearest-neighbor pairs are five-fold bonds, exhibit the highest resistance to shear transformations, while the less-ordered and less-densely packed regions are easier to shear. These results have been used to rationalise the temperature dependence of the elastic limit of Co-B metallic glasses. Amorphous metals do not only exhibit extraordinary mechanical properties, their magnetic properties are equally unique. For example, metallic glasses can be extremely soft magnetically, exhibit gigantic magnetic proximity effects and have even been shown to violate Hund’s third rule. The variations in concentration and coordination number are expected to play similar roles for the magnetic and mechanical properties as e.g. discussed in the analysis of the density, elastic and magnetic properties of CoFeTaB and CoFeTaSi alloys using $ab$ initio theory. This point is also immediate in the different proposed magnetic states in amorphous Fe, depending on the alloying element-induced atomic distances.

While the spatial variation in atomic density and coordination number are used when rationalising the mechanical and magnetic properties of amorphous materials, the experimental determination of these is scarce. The lack of translational and rotational symmetry renders the experimental study of their atomic structure highly challenging: Due to the absence of long range order in amorphous materials conventional diffraction methods yield limited information. Recently, a nano-beam electron diffraction (in a transmission electron microscope) was used to directly observe the local atomic order in a metallic glass. This technique allows the resolution of the local atomic structure, including the determination of local configuration numbers, while it does not provide information on the local density nor spatial variation in the chemical composition.

In an attempt to shed light on the long-standing questions concerning the roots of the physical properties of amorphous materials, we determined the spatial dependence of the composition in Fe$_{1-x}$Zr$_x$ magnetic al-
lois using APT. We grew the materials in thin film form by magnetron sputtering under ultra high vacuum conditions, ensuring good control of the chemical composition as well as the physical extent of the deposited layers. The studied samples were grown on pre-sharpened Si micropits, using two different Fe and Zr target power ratios, resulting in compositions of Fe\textsubscript{0.91}Zr\textsubscript{0.09} and Fe\textsubscript{0.81}Zr\textsubscript{0.19}. For more detailed description of the growth and characterisation of the samples, see Methods.

A typical reconstruction of the elemental distribution is shown in Figure 1. Since the samples were deposited on a pre-sharpened Si tips, the interfaces between the layers are curved, reflecting the initial surface geometry. The red parts in the illustrations mark the FeZr-layers, the yellowish regions represent the amorphous Al\textsubscript{70}Zr\textsubscript{30} buffer and the blue regions mark the partially oxidised Al\textsubscript{70}Zr\textsubscript{30} capping layers. The cubic volumes marked in the FeZr layers define the regions used to determine the elemental distributions within the samples. The measured Zr distribution is displayed as cubes in the top of the figure, within which the difference in the Zr-density of the samples is easily seen. When the local concentration of Fe is displayed in a similar way, the (high-) Fe density hinders any meaningful comparison between the samples. Thus, to illustrate the obtained distributions of Fe we need to invoke a different approach: We averaged the Fe concentration across 2 nm thick segments, thin enough to avoid severe blurring of the lateral changes in the composition, while providing statistically significant results, as illustrated in Figure 2. Experimental contour maps are shown on the top (Figure 2 (a) and (c)) while the illustrations at the bottom (Figure 2 (b) and (d)) displays identical analysis of simulated random distributions of the elements (see Methods). Here it becomes clear that a random distribution does not result in homogenous concentrations of the constituents.

The observed length scales in the contour maps are all similar in Figure 2. However the elemental distributions (Fe and Zr) are somewhat different, as e.g. observed in the Fe distribution illustrated in the inset in Figure 3. This is possibly reflecting a contribution from a thermodynamic driving force arising from the concentration dependence in the mixing enthalpy of the elements, which we conclude to be small here. Let us now consider which effect the spatial variation in concentration can have on the magnetic properties of amorphous Fe\textsubscript{1-x}Zr\textsubscript{x} alloys.

When adding a non magnetic element to a ferromagnetic material, the magnetic ordering temperature (T\textsubscript{c}) typically decreases monotonically over a wide concentration range. This effect can be viewed as a consequence of decreased magnetic interactions (J) upon dilution as T\textsubscript{c} \sim J in a homogenous magnetic system. Fe\textsubscript{1-x}Zr\textsubscript{x} alloys exhibit a more complicated dependence, as illustrated in Figure 3, in which a maximum in T\textsubscript{c} is observed, for an Fe concentration of \approx 0.8. We can use these results to calculate the strength of the local magnetic exchange interaction, corresponding to the concentration...
maps illustrated in Figure 2. To do so we make an ansatz: $T_c \sim \langle J \rangle$, where the brackets denote a weighted average with respect to concentration. Thus the determined $T_c$ is assumed to reflect an average exchange coupling dictated by the average concentration. When the variance in concentration is small, then $J \sim \langle J \rangle$. The inset in Figure 3 shows the determined distribution of Fe concentrations within the samples. Although the variance in the distribution is not negligible, we argue the calculations can be used to infer the changes in the local coupling strength.

To ease the comparison, we define the local magnetic interaction, $J_i$, in units of temperature. Based on the above assumptions we calculated the local exchange coupling for both the samples, as illustrated in Figure 4. In these calculations we have used an interpolation and extrapolation for concentrations above 0.93 (see Figure 3). This is not expected to change the interpretation in any qualitative way, although we can not exclude changes (errors) in the calculated values of $J_i$. As seen in the figure, $J_i$ is changing dramatically ($\Delta J_i \approx 130$ K) over short distances in Fe$_{0.91}$Zr$_{0.09}$, forming twinned magnetic regions, resembling the contour maps of the elemental concentrations. The magnetic properties can therefore not be viewed as being homogenos, even on the length scale of few nm. The results obtained from the Fe$_{0.81}$Zr$_{0.19}$ sample are illustrated in the right hand part of Figure 4. The range in $J_i$ is much smaller ($\Delta J_i \approx 46$ K) as compared to Fe$_{0.91}$Zr$_{0.09}$. The change in effective exchange coupling with concentration ($\delta J/\delta c$) is therefore the signature of how corrugated the energy landscape will be. These changes in magnetic interactions must therefore be reflected in e.g. the changes in the spontaneous magnetization with temperature and we would expect the largest effects to be seen in Fe$_{1-x}$Zr$_x$ samples when $x \lesssim 0.7$ and $x \gtrsim 0.9$. Let us now test these ideas by comparing the magnetic properties of thin amorphous layers and their single element crystalline counterparts. The ordering temperature of magnetic and structural phase transitions in thin layers are found to scale with the thickness ($n$)\(^{37}\) and can be described as:

$$T_c(n)/T_c(\infty) = (1 - \frac{1+2\Delta n}{n})^\lambda,$$

where $\Delta n$ is the extension of a “dead” layer at each interface, $\lambda$ is an exponent and $T_c(\infty)$ is the ordering temperature of bulk (infinitely large) sample. Typical results obtained from crystalline and amorphous materials are illustrated in Figure 5. The results obtained from crystalline Co and Ni on Cu\(^{28}\), as well as Fe$_{0.68}$Co$_{0.24}$Zr$_{0.08}$\(^{29}\) layers are reasonably linearized over a wide range in this representation ($1/n$). The changes obtained from Fe$_{0.90}$Zr$_{0.10}$\(^{30}\) layers, exhibit completely different behaviour, with $\lambda = 0.16\pm0.04$ as compared to $\lambda \approx 1$ for the other layers. This is not surprising when considering the extreme variation of the effective coupling strength within the Fe$_{0.91}$Zr$_{0.09}$ samples. Extrapolating the thickness dependence of $T_c$ for the Fe$_{0.68}$Co$_{0.24}$Zr$_{0.08}$ layers\(^{29}\), results in a $T_c=1025\pm7$ K which is an order of magnitude higher than that of Fe$_{0.90}$Zr$_{0.10}$. Hence although the concentration dependence of $T_c$ is not known, we can safely conclude that $\delta J/\delta c$ is at least an order of magnitude larger in Fe$_{0.90}$Zr$_{0.10}$ as compared to Fe$_{0.68}$Co$_{0.24}$Zr$_{0.08}$. This observation provides the basis for the obtained differences and consequently Fe$_{0.90}$Zr$_{0.10}$ can only be regarded as magnetically continuous well below its ordering temperature.

FIG. 4. Changes in the effective coupling strength with concentration in the Fe$_{0.91}$Zr$_{0.09}$ (left) and Fe$_{0.81}$Zr$_{0.19}$ (right) alloys, expressed as $T_{c,i}$. Large difference is inferred in the effective exchange coupling as a consequence of the nonlinear dependence on concentration. The contour lines in both colormaps depict isolines with an interval of $\Delta T_{c,i} = 20$ K.
The extension of the “dead” layers, $\Delta n$, is significantly different for crystalline and amorphous samples as seen in Figure 5. While crystalline single-element samples typically exhibit a ferromagnetic behaviour to the monolayer limit, amorphous layers lose their spontaneous magnetisation at thicknesses which are almost an order of magnitude larger. The large $\Delta n$ in amorphous alloys is readily rationalised when considering the changes in the effective exchange coupling, reflected in the variation of $J$ within the samples (see Figure 4). Above the apparent $T_c$, the amorphous layers will not be paramagnetic: There will be regions with substantial moments, albeit fluctuating, and thereby not contributing to the spontaneous magnetisation. These are separated by sections with a weaker exchange coupling, effectively decoupling the intrinsically ferromagnetic regions. This interpretation is confirmed by the field dependence of the magnetisation of Fe$_{0.90}$Zr$_{0.10}$, which resembles a super-paramagnetic like behaviour well above $T_c$. The effect is illustrated in the inset in Figure 5, in which a field of $1\, \text{mT}$ is seen to induce a moment which is approximately one half of what is obtained at $80\, \text{K}$. The range of the magnetic correlation in these layers, was estimated to be of the order of $100\,\text{nm}^{30}$ at $T= T_c+20\, \text{K}$, which is substantially larger than the length scales of the compositional contours observed here. Thus, well above the ordering temperature there are large regions within which the variations in $J$ are partially suppressed by magnetic proximity effects.$^{17}$ Furthermore, the large magnetic susceptibility observed in a wide temperature range below $T_c$, reflects the distribution in $T_c$. Finally, when the thickness of the amorphous layers is smaller or equal to $2\Delta n$, a superparamagnetic behaviour is observed at $5\, \text{K}$. Similar effects are observed in Fe$_{0.68}$Co$_{0.24}$Zr$_{0.08}$ layers.$^{29}$ The results presented here provide therefore a base for the understanding of the ordering and phase transitions in amorphous alloys, including finite size effects upon magnetic ordering.

In this communication, we have used the magnetic properties of amorphous materials to demonstrate the consequences of random changes in the local concentration on the magnetic properties of Fe$_{1-x}$Zr$_x$ amorphous alloys. Extending on the experimental results presented here, the extraordinary mechanical properties of amorphous alloys$^{15,32}$ can be argued to stem from the same roots. Recently, it was noted that atomic arrangements and the related probability distributions for particle displacements, can be correlated with string-like excitations. These have a significant impact on the structural relaxation, atomic rearrangement and mechanical properties of metallic glasses.$^{33}$ Having access to direct information on the atomic arrangements, such as obtained when using APT, can therefore shed light on a series of open questions concerning the physical properties of amorphous alloys$^{34}$. The analogy to magnetic properties is straightforward: Replacing the magnetic interactions with chemical binding, results in spatial variation of atomic interactions and thereby causes changes in local elastic properties. Finally, suitable order parameters have been proposed within the framework of mean-field theory, such as the overlap function $Q$, for which an experimental determination requires detailed and atomically resolved structural information.$^{35}$

Obtaining a better understanding on the role of elemental distributions in amorphous alloys will enable the tailoring of physical properties, not accessible in homogenous materials. Our findings exemplify a new route, using directly determined experimental structural and statistical quantities for amorphous and glassy systems, being directly linked to fundamental physical and thermodynamic properties. These can be utilised to refine and further enhance our understanding of amorphous materials and its liaison with the observed macroscopic physical properties. We also note the lack of a theoretical framework, for both the effect of non-homogenous interactions and especially its influence on the emergent order in finite size systems. However, to implement realistic descriptions of amorphous alloys we need to recognise that random compositions are intrinsically inhomogeneous in nature.
doubtedly atomic classification, the signal at m/e = 27 is removed in the data evaluation processes because of the mass overlap of Fe and Al ($^{56}$Fe$^{2+}$ and $^{27}$Al$^{3+}$) in the seeding and capping layers. This approach was not implemented in the analyses of the Fe-Zr layers.

A random FeZr alloy with the same volume and nominal composition was simulated and investigated for comparison, by using Region of Interest (ROI) simulation tool of the same software. The simulation of the volume assumed a bcc lattice. We, therefore, included a 0.5 nm smearing of the data to better mimic the amorphous alloys. The detection efficiency was set to 0.36, which is a typical value for the LEAP 4000 with reflectron. The detection efficiency has pure geometrical reasons and is therefore assumed to be insensitive to the detected elements$^{87}$. The chosen density $\rho$ in atoms per nm$^3$ was adjusted to the best match value in a respective volume to that of the measured counterpart. The density $\rho = 77.82$ atoms nm$^{-3}$ for Fe$_{91}$Zr$_{0.9}$, $\rho = 79.86$ atoms nm$^{-3}$ for Fe$_{91}$Zr$_{0.9}$, respectively. Typical depth profiles are shown in figure 6 for a) Fe$_{91.91}$Zr$_{0.09}$ and c) Fe$_{90.91}$Zr$_{0.09}$ samples. The Zr depth profiles shown in figure 6 a) provide the matching average concentration of 9 at.% Zr for the alloy, as given by the dashed black line. Some local concentration values exceed the doubled standard deviation (2 $\sigma$-value, marked with the red dotted lines) of the average Zr concentration. This is also observed for the simulated random alloy. Our observation is consistent with a slight thermodynamically driven composition variations in the alloy.

**Methods**

Sample growth and characterization

Amorphous FeZr thin films have been deposited by DC magnetron sputtering from elemental targets at room temperature. The base pressure was below $5 \times 10^{-6}$ mbar and the (purified) Ar pressure during growth was 4 - $10^{-3}$ mbar. Since FeZr thin films on Si substrates grow partly crystalline at room temperature$^{36}$ an amorphous AlZr seed layer was deposited from an Al$_7$Zr$_{25}$ compound target. The same target was used to deposit a capping layer to avoid oxidation of the magnetic layers. For APT, layers were deposited directly on pre-sharpened Si micro-tips with two different Fe and Zr target power ratios, resulting in compositions of Fe$_{91}$Zr$_{0.9}$ and Fe$_{91.91}$Zr$_{0.91}$. The chemical compositions were confirmed by energy dispersive X-rays as well as atomic probe analysis.

APT analyses were carried out on LEAP 4000 XHR (Cameca) in laser pulsing mode using a laser wavelength of 355 nm, a laser energy of 70 pJ, a pulse repetition rate of 200 kHz, with a detection rate of 0.003 ions per pulse. The sample temperature was set to 70 K in these measurements. As the pulse method always removes the particular uppermost surface atoms, the depth resolution of this APT analysis is one atomic layer. The lateral resolution within the layer is about 0.5 nm$^{37}$.

The 3-D reconstruction of the ion positions was performed using IVAS 3.6.6 (Cameca). The initial radius of curvature $r_0$ and the specimen’s shank half angle $\theta$ were determined by scanning electron microscope (SEM) (Helios, FEI) before the analysis and later applied in the reconstruction process. In both the amorphous alloys typical values of $r_0$ and $\theta$ were found to be $r_0 = 30$ nm and $\theta = 16^\circ$, respectively. After the reconstruction, the 1st FeZr layer was chosen for evaluation of the chemical homogeneity by studying the concentration histogram, by using the ‘cluster search’ and the ‘concentration mapping’ provided by IVAS 3.6.6. To allow for...
ACKNOWLEDGMENTS

This work was funded by the Swedish Research Council (VR), Foundation of Strategic Research (SSF), the Knut and the Alice Wallenberg foundation (KAW). Work undertaken at the KAUST was supported by the King Abdullah University of Science and Technology (KAUST). A.P. was supported by the Deutsche Forschungsgemeinschaft in the Heisenberg program via PU131/9-2.

AUTHOR CONTRIBUTIONS

B.H., M. B. and A.P. designed the experiment. M.B., A.P. and R.G. carried out the APT sample preparation. R.G. carried out the APT measurements. R.G. and A.P. performed the APT data analysis. All authors contributed to the interpretation of the results and the writing of the manuscript.

AP and RG thank Dr. T. Boll (KNMF at KIT) for kind discussion.

* Present address: Department of Materials Science, Tokai University, Japan
† Present address: GTT-Technologies, Kaiserstr. 103, 52134 Herzogenrath, Germany
‡ bjorgvin.hjorvarsson@physics.uu.se

1 W. Buckel and R. Hilsch, Zeitschrift für Physik 131, 420 (1952).
2 W. Klement, R. H. Willens, and P. Duwez, Nature 187, 869 (1960).
3 A. L. Greer, Science 267, 1947 (1995).
4 C. A. Angell, Science 267, 1924 (1995).
5 K. H. J. Buschow and P. H. Smit, Journal of Magnetism and Magnetic Materials 23, 85 (1981).
6 M. Ahlberg, P. Korelis, G. Andersson, and B. Hjörvarsson, Phys. Rev. B 85, 224425 (2012).
7 M. Ahlberg, A. Zamani, E. Östman, H. Fashandi, B. Hjörvarsson, and P. E. Jönsson, Phys. Rev. B 90, 184403 (2014).
8 F. Magnus, M. E. Brooks-Bartlett, R. Moubah, R. A. Procter, G. Andersson, T. P. A. Hase, S. T. Banks, and B. Hjörvarsson, Nature Communications 7, 11931 (2016).
9 H. S. Chen, Reports on Progress in Physics 43, 353 (1980).
10 M. Dao, L. Lu, R. Asaro, J. D. Hosson, and E. Ma, Acta Materialia 55, 4041 (2007).
11 A. L. Greer and E. Ma, MRS Bulletin 32, 6117619 (2007).
12 A. Inoue, K. Ohtera, K. Kita, and T. Masumoto, Japanese Journal of Applied Physics 27, 12248 (1988).
13 M. D. Demetriou, M. E. Launey, G. Garrett, J. P. Schramm, D. C. Hofmann, W. L. Johnson, and R. O. Ritchie, Nature Materials 10, 123 (2011).
14 L. Zhang, Y.-Q. Cheng, A.-J. Cao, J. Xu, and E. Ma, Acta Materialia 57, 1154 (2009).
15 Y. Q. Cheng, A. J. Cao, H. W. Sheng, and E. Ma, Acta Materialia 56, 5263 (2008).
16 V. Schnabel, J. Bednarick, D. Music, T. Pazur, C. Hostert, and J. M. Schneider, Materials Research Letters 3, 82 (2015).
17 F. Magnus, R. Moubah, U. B. Arnalds, V. Kapaklis, A. Brunner, R. Schäfer, G. Andersson, and B. Hjörvarsson, Phys. Rev. B 89, 224420 (2014).
18 V. Kapaklis, P. T. Korelis, B. Hjörvarsson, A. Vlachos, I. Galanakis, P. Poulopoulos, K. Özdoğan, M. Angelakeris, F. Wilhelm, and A. Rogalev, Phys. Rev. B 84, 024411 (2011).
19 C. Hostert, D. Music, J. Bednarick, J. Keckes, V. Kapaklis, B. Hjörvarsson, and J. Schneider, Journal of Physics: Condensed Matter 23, 475401 (2011); C. Hostert, D. Music, V. Kapaklis, B. Hjörvarsson, and J. M. Schneider, Scripta Materialia 66, 765 (2012).
20 H. U. Krebs, D. J. Webb, and A. F. Marshall, Phys. Rev. B 35, 5392 (1987).
21 G. Xiao and C. Chien, Physical Review B 35, 8763 (1987).
22 I. Bakonyi, Journal of Magnetism and Magnetic Materials 324, 3961 (2012).
23 A. Hirata, P. Guan, T. Fujita, Y. Hirotsu, A. Inoue, A. R. Yavari, T. Sakurai, and M. Chen, Nature materials 10, 28 (2011).
24 P. Sharma, H. Kimura, and A. Inoue, Phys. Rev. B 78, 134414 (2008).
25 D. Read, T. Moyo, and G. Hallam, Journal of Magnetism and Magnetic Materials 54-57, 309 (1986).
26 P. Korelis, Uncovering Magnetic Order in Nanostructured Disordered Materials : A Study of Amorphous Magnetic Layered Structures, Ph.D. thesis, Uppsala University, Materials Physics (2011).
27 X. Xin, G. K. Pålsson, M. Wolff, and B. Hjörvarsson, Phys. Rev. Lett. 113, 046103 (2014).
28 F. Huang, M. T. Kief, G. J. Mankey, and R. F. Willis, Phys. Rev. B 49, 3962 (1994).
29 M. Ahlberg, G. Andersson, and B. Hjörvarsson, Phys. Rev. B 83, 224404 (2011).
30 P. T. Korelis, P. E. Jönsson, A. Liebig, H.-E. Wannberg, P. Nordblad, and B. Hjörvarsson, Phys. Rev. B 85, 214430 (2012).
31 A. Liebig, P. T. Korelis, M. Ahlberg, and B. Hjörvarsson, Phys. Rev. B 84, 024430 (2011).
32 H. W. Sheng, W. K. Luo, F. M. Alamgir, J. M. Bai, and E. Ma, Nature 439, 419 (2006).
33 H.-B. Yu, R. Richert, and K. Samwer, Science Advances 3, e1701577 (2017).
34 L. Berthier and G. Biroli, Reviews of Modern Physics 83, 587 (2011).
35 L. Berthier and M. D. Ediger, Physics Today 69, 40 (2016).
36 P. T. Korelis, A. Liebig, M. Björck, B. Hjörvarsson, H. Lidbaum, K. Leifer, and A. Wildes, Thin Solid Films 519, 404 (2010).
37 T. F. Kelly and M. K. Miller, Review of Scientific Instruments 78, 031101 (2007).