Full length article

Density power law and structures of metallic glasses

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ABSTRACT

The existence of a universal power law relating the position of the first sharp diffraction peak (q, FSDP) to the density (ρ or the volume V) with a constant exponent <3 has been debated in the last decade. A constant dimensionality is important because it reflects the fractal topology of the glass structures. In this study, the validity of the Ehrenfest equation applied to multi-component metallic glasses is examined using first-principles molecular dynamics calculations. The results show that the Ehrenfest coefficient depends on the local structures of the glasses and is not a constant for all glasses. Moreover, since the diffraction pattern is determined by the scattering between atom pairs, in a multi-component glass, the X-ray diffraction FSDP is only sensitive to the heavy atoms, and the observed P-q relationship does not necessary correspond to the P–V equation of state of the bulk material and is not always a suitable indicator for monitoring structural phase transitions or volume changes. On the other hand, for suitable systems, neutron diffraction is a reliable method to determine the structural features of both heavy and light atoms. In this study, the simulated neutron diffraction patterns of $Ca_{72.7}Al_{27.3}$ metallic glasses show a clear splitting of the FSDP at the pressure where the pressure-induced polyamorphism transition occurs. From the presented results, there is no justification for expecting the existence of a universal power scaling law with a constant exponent for all glasses.

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1. Introduction

Metallic glasses have attracted intense attention because of their superior properties, such as high strength, hardness, elasticity, high corrosion resistance and unique magnetic properties [1–7]. However, these materials also display several shortcomings, such as low glass forming ability and low production efficiency that have hindered the wider applications of such materials. To further improve the properties of metallic glasses, especially those of multi-component systems, it is essential to acquire an understanding of the glass structures at the atomistic level. To explore the configuration space, it is useful to establish empirical rules of property-property and property-structure correlations. In practice, correlations between properties are often easy to derive from experimental data. For example, quantitative correlations have

been established between ductility, fragility and Poisson's ratio for a number of metallic glasses [2]. On the other hand, the validity of property-structure correlations is much more difficult to assess due to the lack of knowledge of the micro-structures of metallic glasses caused by experimental difficulties.

Despite the complication of disorder, diffraction using X-rays (XRD) or neutron is by far the most often used technique for the characterization of the structures of metallic glasses. The diffraction patterns (structure factors $S(q)$) of the different metallic glasses are often similar, with the position of the first sharp diffraction peak (FSDP) located at $q = 2$–3 Å^{-1}. The interplanar d-spacing, $d = 2\pi/q$, has been found to be close to the first-neighbor atomic distance [8]. This observation has often been used to justify the use of the well-known Ehrenfest relationship [9],

$$q = 2\pi k/r \qquad (1)$$

where k is a proportionality constant (Ehrenfest coefficient) relating the shortest interatomic distance to the position of the FSDP. Recently, a q-r correlation was found by the combination of a nanobeam electron diffraction experiment and *ab initio* molecular

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dynamics simulations for the $Zr_{66.7}Al_{33.3}$ metallic glass [10]. The question is whether this relationship with a "universal" k is applicable to all glasses. If the Ehrenfest relationship is transferable to different metallic glasses and the shortest interatomic distance scales with the volume, then a general density power scaling law is expected, as given by

$$\frac{V_0}{V_1} = \frac{\rho_1}{\rho_0} = \left(\frac{kq_1}{kq_0}\right)^D = \left(\frac{q_1}{q_0}\right)^D \qquad (2)$$

Here, the subscripts 0 and 1 represent the reference structure and the target structure, respectively. The power factor D should be equal to 3 if the disordered structure is macroscopically isotropic. This is because an isotropic disordered structure can be regarded as a cubic cell with an infinitely large lattice constant a. It is not unreasonable to assume that the variation of the interatomic distance d is proportional to a, so that the cell volume can be described as $V = a^3 \propto d^3$. From the analysis of a selected set of metallic glass at ambient pressure, Ma et al. reported a power constant of 2.31 [11]. This unexpected scaling factor introduced a new perspective on the structural dimensionality and the fractal geometry that may have important implications for the glass structures. However, this scaling factor was later found not to be rigorous. Cheng et al. demonstrated that the power scaling constant of 2.31 is not universal and the value can vary for different metallic glasses or liquids with different atomic packing topologies [2]. For instance, a value of 2.658 was obtained by fitting data for the Cu_xZr_{100-x} metallic glasses [2,12]. Gangopadhyay et al. [13] reported the breakdown of Ehrenfest's relation in alloy liquids from the thermal expansion measurements by x-ray scattering, and a density scaling factor value of 2.28 was fitted from the collected data. Recently, Zeng et al. [8] and Chen et al. [14] suggested another power scaling constant of 2.5 in compressed metallic glasses. More surprisingly, this rule apparently even holds in Ce-based glasses that are known to undergo polyamorphism structural transitions under pressure [8,14]. The contradictory and inconsistent results deepen the controversy regarding a universal structure-property correlation for metallic glasses. A closer re-examination of the data of Zeng et al. [8] shows that different values of the power scaling constant can also be extracted for different systems, even though all of these are very close to the proposed value of 2.5. To establish the fractal characteristics of metallic glasses, extensive sets of highly accurate experimental data are required. Moreover, one fundamental question that needs to be considered is the general applicability of the Ehrenfest relationship in metallic glasses. Therefore, the purpose of the present investigation is to examine the validity of the correlation between the position of the FSDP (q) and the density of multicomponent metallic glasses under pressure.

The Ehrenfest equation central to the present issue and the q-r relationship have already been analyzed in detail in Guiner's classical book on the powder diffraction of amorphous solids It was shown that for amorphous solids the expression

$$q = (2\pi \times 1.23)/r \qquad (3)$$

holds as long as the effective volume (i.e., the sum of the atomic volumes) is much smaller than the total volume. It was further asserted that the relationship is only applicable to monoatomic gaseous systems and not to polyatomic solids [9]. In addition, the constant k in equation (1) is expected to have different values for different solids. For instance, the theoretical values of k are 1.22, 1.23 and 1.15 for the face-centered cubic (FCC), the body-centered cubic (BCC) and the close-packed hexagonal (HCP) structures, respectively. The large difference in the k values between the FCC and HCP structures is noteworthy in view of the equivalent sphere

packing densities for these structures. While for compressed metallic glasses, the structures are often assumed to be already close-packed, it has been proven both theoretically and experimentally that the local structures can change under compression [15,17]. In a previous study of the $Ca_{72.7}Al_{27.3}$ metallic glass, a polyamorphic transition with an unexpected increase in coordination numbers was found and characterized [18,19]. Therefore, it is highly doubtful that the Ehrenfest coefficient k would remain constant under different structural environments. If a "magic number" for the power scaling constant (e.g., 2.5) does not exist in compressed metallic glasses, this implies that the $P–V$ equation of state is not equivalent to the P-q relationship. In other words, one cannot rely solely on the observed variation in the P-q curve as the proof for a structural phase transition. This procedure is commonly used in the study of glasses and other disordered solids. As mentioned above, the values of the theoretical Ehrenfest coefficient k for ideal monoatomic FCC, BCC and HCP structures are different and are apparently close to the value of 1.23 (eqn. (3)) obtained for a disordered system. However, a 4% deviation in k will be amplified to the volume difference of 12% ($1.04^3 – 1.0$). This volume difference is significantly larger than the volume change usually associated with a typical polyamorphic transition in metallic glasses.

First-principles molecular dynamics calculations (FPMD) have proven to be reliable for reproducing the structures of many metallic glasses [10,15]. In our previous FPMD studies on the amorphous systems including metallic glasses and silica glasses, despite the relative small unit cell employed in the calculations (100–200 atoms), the calculated $S(q)$ or the FSDP agree very well with the experiment results (Supplementary Material Fig. S1). The reason being that the position of FSDP q has an inverse relationship with the "interplanar" distance d, $q = 2\pi/d$. Since the FSDP positions of the metallic glasses considered in the present study are around 2–3 Å^{-1}, i.e. the interplanar distances contributing to the FSDP is about 2–3 Å. As supercells of about 10 Å were used in the simulations, due to the use of periodic boundary conditions, the interatomic distance is reliable up to half of the model cell or around 5 Å. In the present work, FPMD calculations were performed on three X–Al (X = Ce, Ca and La) metallic glasses with similar stoichiometries but very different behaviors under pressure in order to examine the Ehrenfest relationship and the fractal characteristics of the glasses. In particular, the $Ce_{75}Al_{25}$ metallic glass has been found to undergo a structural transition at 1.5–5 GPa attributed to the Ce $4f \rightarrow 5d$ rehybridization and then transform to a crystalline FCC solid solution at 25 GPa [20]. The main group $Ca_{72.7}Al_{27.3}$ metallic glass also shows a polyamorphism transition due to the change of chemical bonding between the Ca $3d$ and Al $3p$ orbitals [19]. To date, no polyamorphism transition has been reported in the $La_{75}Al_{25}$ metallic glass even though it has been speculated that the local atomic environment may change continuously under compression [21]. In the following, a systematic comparison of the theoretical results obtained for these three systems will be presented and discussed. The goal is to examine the Ehrenfest relationship to either confirm or refute the existence of a universal power scaling law in compressed metallic glasses.

2. Methods

FPMD calculations of the metallic glasses were performed with the *Vienna Ab initio Simulation Package* (VASP) based on the density functional theory [22,23]. Interactions of the valence and core electrons were represented by projected augmented wave (PAW) potentials [24]. Valence electronic configurations of $5s^25p^6\mathbf{4f^15d^16s^2}$, $3s^23p^64s^2$, $5s^25p^6\mathbf{5d^16s^2}$ and $3s^23p^1$ were used for Ce, Ca, La and Al, respectively. Since the DFT method fails to describe the localized $4f$ electronic state under ambient pressure