様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

# 科学研究費助成事業　　研究成果報告書

令和　５ 年　 ６ 月　 ６ 日現在

機関番号：８２１１０
研究種目：研究活動スタート支援
研究期間：2021～2022
課題番号：２１Ｋ２０４１８

研究課題名（和文）Establishment of deformation law of metallic glasses based on local atomic level analysis

研究課題名（英文）Establishment of deformation law of metallic glasses based on local atomic level analysis

研究代表者

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交付決定額（研究期間全体）：（直接経費）　　2,400,000円

研究成果の概要（和文）：金属ガラスのひずみ下での挙動に関して、巨視的な力学特性と微視的な応答との間のギャップは理解されていない。本研究では、CuZrアモルファス系を例に、第一原理計算の枠組みの原子応力計算を用いて金属ガラスのせん断歪みに対する応答を評価する手法を構築した。その結果、ガラスのCuとZrのサブシステムは、フォンミーゼス応力、電荷移動、フェルミレベルの電子部分状態密度の変化などの局所パラメータの評価が、ひずみ下の力学応答を理解する強力なツールとなることがわかった。とりわけ、原子フォンミーゼス応力は、D2min（各原子の線形歪みからの偏差）との相関が強いことを示し、その意義を明らかにした。

研究成果の学術的意義や社会的意義
本研究は、一般的な古典的分子動力学（MD）シミュレーションよりも信頼性の高い密度汎関数理論（DFT）の手法を用いた高精度な第一原理計算によって実施されたものである。このような枠組みでは使われることのなかった原子応力計算に基づくvon Mise応力を計算し、このパラメータが古典的MDで得られた結果と比較できることを示す。一般的に用いられるせん断応力とは対照的に、von Mises応力はすべての応力成分の変化を捉えることができるため、不均質性の高い系に対してより信頼性が高い。CuZrの力学的挙動の理解により、材料の劣化について予見することが可能となることから、意義を有している。

研究成果の概要（英文）：The behavior of metallic glass under strain is not fully understood yet due to its essentially emergent nature, and the gap between macroscopic mechanical properties and the microscopic responses remains open. In this study, we employ a unique technique of atomic stress calculations in the first principles framework to build a comprehensive picture of metallic glass response to the shear strain using the CuZr amorphous system as an example. The Cu and Zr subsystems of the glass were found to be different in developing the response by examination of the local parameters, among which are von Mises stress, charge transfer, and change of electronic partial density of states at the Fermi level. We show the significance of atomic von Mises stress by showing its stronger correlation with D2min (deviation from the linear strain on each atom). Overall the behavior of CuZr metallic glass under shear strain is thoroughly described in this study from mechanical and electronic points of view.

研究分野：Computational Materials Science

キーワード：Metallic glass　Atomic stress　First-principles

## １．研究開始当初の背景

Amorphous materials have been the subject of extensive research over the past few decades due to their unique properties. As such, metallic glasses (MGs) demonstrate high mechanical strength, hardness, and corrosion resistance. Unlike crystals, where the dynamics of well-defined dislocations govern plastic deformation, MGs respond to the external strain with the activation of collective atomic motion usually referred to as the shear transformation zone (STZ). All attempts to find pre-existing sources that would trigger STZ have not been successful so far, and the deformation in MGs is believed to be of an essentially emergent nature. Many experiments and simulations show discrepancies regarding the size of STZs, which could be mainly attributed to the stability of samples with different thermal treatments, limitations dictated by experimental equipment, such as the size of the nanoindentation chip, and the choice of local structural parameters explored in simulations. Moreover, STZs structure changes with the development of the deformation, which complicates its studies. Thus, revealing the atomistic origin of the mechanical properties of MGs has been a long-standing problem in physics and material science, and the gap between macroscopic mechanical properties and the microscopic responses remains open.

## ２．研究の目的

Computer modeling can provide theoretical insights into the properties of STZ. The commonly employed approach both in Japan and overseas is classical molecular dynamics (MD), with an empirical potential to mimic realistic deformation behaviors. However, with the recent achievements of modern computational techniques, the deformation behavior can be studied using one of the most accurate methods - first-principles modeling based on the density functional theory (DFT). In this study, we apply DFT calculations to the CuZr metallic glass systems and draw a connection between its local mechanical response and the electronic state under shear strain. Because of the use of the unique technique of calculating atomic stress in DFT, we combine previously achieved classical MD results and the new data from the electronic sub-system, which cannot be obtained in classical simulations. Subsequently, we aim to build a comprehensive set of local parameters of MG along with correlations between them to unveil the atomic level mechanisms of the stress response (e.g., well-known shear softening of MG). An understanding of the mechanical behavior of CuZr may help prevention of unexpected failure in applications.

## ３．研究の方法

It is known from the classical MD simulations that atomic stress is a vital parameter indicating the mechanical state of the system. Atomic stress calculations have been used extensively to describe the disordered structures of liquids and glasses or to characterize mechanical behaviors of the atomic environment, such as the occurrence of localized events and the growth of elastic fields. In contrast to classical atomic stresses, its calculations in first principles are not common because of difficulties in implementation and uncertainties in the definition. In this study, we employ the linear combination of atomic orbitals (LCAO) scheme, which allows one to separate the contributions of particular atoms to the total energy in DFT. That leads to a straightforward definition of atomic stress as a derivative of atomic energy with strain. Atomic stress calculations allow us to compare results with a large number of other studies previously carried out with classical MD while adding unique data from the electronic sub-system. The structures of amorphous CuZr are obtained with the fast-quenching scheme mimicking in DFT the real process of MG specimen preparation. We perform athermal quasi-static shear (AQS) simulation for its well-known ability to show the mechanical response of the system in simulations. This study is focused on the system change from the affine to the relaxed state under shear strain. We use the change of atomic von Mises stress ($\Delta\sigma^{k}_{vM}$, where k stands for an atom number) as one of the main indicators of such change. The uniqueness of results is assured by the fact that $\Delta\sigma^{k}_{vM}$ has never been previously calculated for MG structures in DFT, while its importance is shown in our results. To build a comprehensive picture of CuZr MG response to the shear strain, we also calculate the

following parameters: $D^2_{min}$ showing the atoms with displacements that deviate substantially from the linear ones; change in the Bader charges associated with each atom; change in partial electron density of states (PDOS); individual coordinate change (Δr); coordination number (Nc) based on chemical bonds. These parameters are collected for each atom for further analysis of correlations between them.

## 4．研究成果

(1) Correlations between local parameters in CuZr MG initial state

To characterize the stress state on the atomic level, we start by examining the components of atomic stress matrices. The atomic pressure indicates differences between the Cu and the Zr sub-systems of the glass. Cu atoms are in a tensile state (negative pressure), while Zr atoms are under compression (positive pressure). It is not a surprise that in an alloy, the pressure on atoms of different species bifurcates from zero into opposite directions due to the volume mismatch. Our calculations of the Bader charge ($Q_{Bader}$) for each atom show that the transfer of charge (difference of the charge on a particular atom in the glass and its total number of valence electrons as defined by the pseudo-potential) correlates with atomic pressure in the initial state of CuZr structures (see Fig. 1(a)).

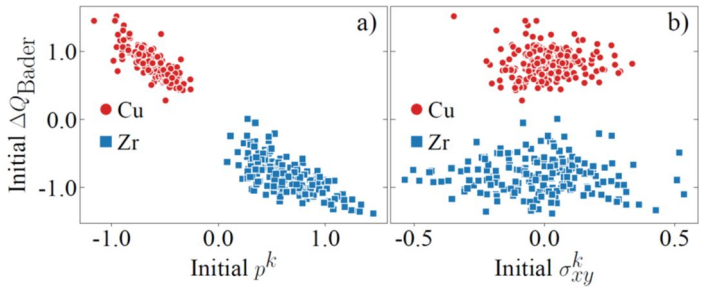


Fig. 1 Relation between the charge transfer ($\Delta Q_{Bader}$) in the initial state of CuZr MG and (a) atomic pressure, (b) atomic shear *xy* stress.

Another parameter that can reveal information about the system's initial state is the coordination number (Nc). We derive it from the Bader analysis, which can give the chemical bonds between atoms as the critical points of the charge density scalar field (the points where the field's gradient vanishes). Obtained Nc differs from the topological coordination number used in classical MD, as the latter depends on the cut-off radius predefined for each atom specie. Therefore, we refer to Nc as a chemical coordination number. The relation of Nc and atomic pressure ($p_k$) is shown in Fig. 2. The results for the coordination number using only different type neighbors ($Nc^{(other)}$), shown in Fig. 2(b), reveal the tendency for Zr atoms with a higher number of bonds with Cu atoms to have more considerable pressure so that such Zr atoms are in a more compressed state. That can be explained by the smaller volume associated with a Zr atom if it forms many bonds with Cu atoms.

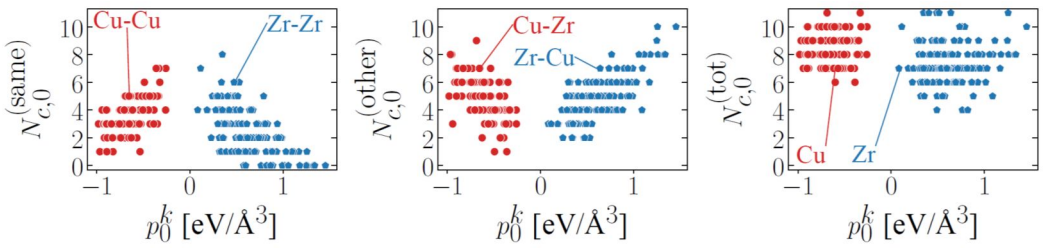


Fig. 2 Relation between the chemical coordination number ($N_c$) in the initial state of CuZr MG: (a) same-type bonded neighbors, (b) other-type bonded neighbors, (c) $N_c$ based on all bonded neighbors.

(2) Correlations between local parameters in CuZr MG under shear strain

The *xy* stress component of atoms in CuZr glass under shear strain behaves differently for Cu and Zr sub-systems: Zr atoms demonstrate a positive stress response in the affine state under strain, but Cu atoms exhibit the negative one. Such a negative shear modulus of Cu in MG is not seen in classical simulations, making comparing results impossible. On the other hand, the atomic von Mises stress ($\Delta\sigma^k_{vM}$) calculated in the current study from first principles demonstrates a more natural behavior because of the fact that $\Delta\sigma^k_{vM}$ is invariant under rotations, and it captures the change of all components of the atomic stress matrix. Presented in Fig. 3 are the Pearson correlation coefficients (PCC) calculated for all atomic parameters indicating the change between affine and relaxed states of CuZr MG under shear strain. Our DFT results show a correlation between atomic displacement and atomic von Mises stress change. We also found the correlation between $\Delta\sigma^k_{vM}$ and the well-known $D^2_{min}$ parameter induced by the system's relaxation under shear strain. That shows the importance of the $\Delta\sigma^k_{vM}$ parameter for analysis of the mechanical response on an atomic level in MG. The analysis of the electronic sub-system reveals that its change has a weak correlation with the mechanical response: atoms with larger von Mises stress tend to have larger change in electronic partial density of state near the Fermi level.

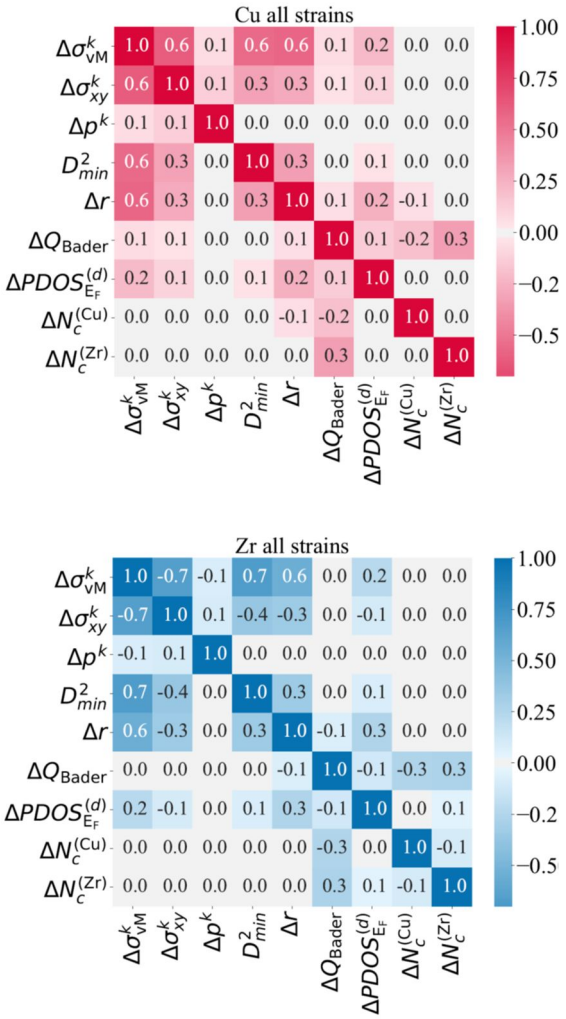


Fig. 3 Correlation coefficients between the parameters indicating the system transformation between affine and relaxed states under shear strain.

５．主な発表論文等

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| オープンアクセス<br>オープンアクセスではない、又はオープンアクセスが困難 | 国際共著<br>－ |

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| オープンアクセス<br>オープンアクセスとしている（また、その予定である） | 国際共著<br>－ |

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| オープンアクセス<br>オープンアクセスではない、又はオープンアクセスが困難 | 国際共著<br>該当する |

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| オープンアクセス<br>オープンアクセスではない、又はオープンアクセスが困難 | 国際共著<br>－ |

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〔図書〕　計0件

〔産業財産権〕

〔その他〕

Research Group for Radiation Materials Engineering
https://nsec.jaea.go.jp/fme/en/group5/group5_index.htm

６．研究組織

| | 氏名<br>（ローマ字氏名）<br>（研究者番号） | 所属研究機関・部局・職<br>（機関番号） | 備考 |
|---|---|---|---|

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

| 共同研究相手国 | 相手方研究機関 |
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