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Anomalous packing state in Ce-Ga-Cu bulk metallic glasses

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ABSTRACT

Formation mechanism of bulk metallic glasses (BMGs) with high glass-forming ability (GFA) has been a long-standing subject in the field of solid state physics. To highlight the GFA-associated local atomic structure, element-specific positron annihilation spectroscopy was conducted for recently discovered ternary $Ce_{70}Ga_xCu_{30-x}$ (x = 6–13; at.%) BMGs. We succeeded in identifying the packing structure under the condition of ambient pressure, in which Ce atoms are concentrated more than that in Ce crystal. This anomalous glassy state is most efficiently formed at the Ga concentration of ~10%, where the best glass-forming ability (GFA) is experimentally observed. First-principles computer simulation results suggest that this anomalous packing structure is associated with Ce-4*f* electron delocalization in the Ce-Ga-Cu BMGs. The findings provide unambiguous evidence for the relationship between the packing-efficient local structure and the GFA.

1. Introduction

Formation mechanism of bulk metallic glasses (BMGs) with high glass-forming ability (GFA) has been a long-standing subject in the field of solid state physics. A great deal of efforts has been devoted to elucidating the GFA of BMGs and especially their composition dependency [1–5]. From a theoretical point of view [6,7], efficient and dense atomic packing is conceptually required for the formation of BMGs with high GFA. Recently, the atomic structure and its correlation with GFA have become one of the central issues in the experimental and computer simulation investigations of BMGs [5,8–11]. However, it is difficult to obtain the exact packing density from conventional structural analyses based on X-ray or neutron diffraction techniques because of the lack of information on the real atomic size due to the complexity of chemical effect in multicomponent alloys.

Positron annihilation spectroscopy has been proven to be capable of investigating vacancies in aperiodic materials such as polymers [12], quasicrystals [13], and BMGs [14–17]. The measurements of positron lifetimes by positron lifetime spectroscopy and momentum distributions of annihilation γ-rays by coincident Doppler broadening (CDB) spectroscopy enable to obtain the information of vacancy size and its local chemical environment, respectively. Positron lifetime spectroscopy for Zr-based multicomponent BMGs alloy systems yielded a single component with the positron lifetime of ~180 ps (see Table 1), signifying the presence of vacancy-sized free volumes higher than 10^{-4} in the atomic concentration [14–17]. The chemical surroundings of vacancy-sized free volumes were found to be dominated by Zr atoms by CDB spectroscopy [16,17].

Polyamorphism upon application of pressure for Ce-based metallic glasses (MGs) has been extensively studied by using X-ray diffraction experiments together with theoretical calculations [18–20]. This phenomenon was observed in binary [21] as well as in ternary and quaternary Ce-based MGs [22,23]. The polyamorphism mechanism was explained as 4*f* electron delocalization in Ce atoms under pressure, which caused bonding shortening and volume shrinkage. Apart from the pressure-induced polyamorphism, recently Tiwari has observed that chemical pressure could also partially trigger Ce-$4f^0$ delocalized state due to Ga substitution in $Ce_{75}Al_{25-x}Ga_x$ MGs [24,25]. Such a substitution of Ga could lead to shortening of Ce-Ce distance owing to chemical pressure.

In this work, the local atomic structures and GFA were studied by element-specific positron annihilation spectroscopy together with theoretical calculations for recently discovered ternary

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Table 1
Positron lifetimes for the present $Ce_{70}Ga_xCu_{30-x}$ ($6 \le x \le 13$) and $Ce_{68}Al_{10}Cu_{20}Nb_2$ BMGs together with those of various amorphous alloys reported until now. Positron lifetimes τ_1, τ_2, τ_3, and τ_4 are ascribed to annihilation at defect-free region, vacancy, nanovoid, and microvoid, respectively, and I_1, I_2, I_3, and I_4 are their corresponding intensities. For comparison, positron lifetimes at defect-free ($\tau_{defect\text{-}free}$) and monovacancy ($\tau_{monovacancy}$) for several pure metals are shown as well.

Glasses	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)	τ_3 (ps)	I_3 (%)	τ_4 (ps)	I_4 (%)
	(defect free)		(vacancy)		(nanovoid)		(microvoid)	
$Ce_{70}Ga_6Cu_{24}$	129.8	16.9	261.0	83.1	–	–	–	–
$Ce_{70}Ga_8Cu_{22}$	130.8	18.3	260.1	81.7	–	–	–	–
$Ce_{70}Ga_{10}Cu_{20}$	129.1	19.2	261.0	80.8	–	–	–	–
$Ce_{70}Ga_{11}Cu_{19}$	130.3	18.4	262.2	81.6	–	–	–	–
$Ce_{70}Ga_{12}Cu_{18}$	128.8	17.4	262.2	82.6	–	–	–	–
$Ce_{70}Ga_{13}Cu_{17}$	129.6	15.8	261.6	84.2	–	–	–	–
$Ce_{68}Al_{10}Cu_{20}Nb_2$	–	–	213	100	–	–	–	–
$Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ [14]	–	–	173.5	100	–	–	–	–
$Zr_{65}Al_{7.5}Ni_{10}Cu_{17.5}$ [15]	–	–	186.4	100	–	–	–	–
$Zr_{52.5}Ti_5Al_{10}Cu_{17.9}Ni_{14.6}$ [16]	–	–	177.0	100	–	–	–	–
$Zr_{50}Cu_{40}Al_{10}$ [17]	–	–	163.0	100	–	–	–	–
$Ni_{36}Nb_{24}Zr_{40}$ [33]	–	–	172.1	100	–	–	–	–
$Fe_{35}Co_{52}V_{13}$ [34]	–	–	161.0	100	–	–	–	–
$Fe_{80}B_{20}$ [35]	–	–	142.0	100	–	–	–	–
$Ni_{81}P_{19}$ [35]	–	–	166.0	100	–	–	–	–
$Cu_{57}Zr_{43}$ [35]	–	–	175.0	100	–	–	–	–
$Fe_{75}P_{16}B_6Al_3$ [36]	–	–	170	97	500	3	–	–
$Ni_{75}P_{16}B_6Al_3$ [36]	–	–	170	97	500	3	–	–
$Fe_{78}B_{13}Si_9$ [37]	–	–	153.4	92.9	399.9	7.1	–	–
$Pd_{77.5}Cu_6Si_{16.5}$ [38]	–	–	169.0	97.5	410	2.5	–	–
$Fe_{64}Co_{21}B_{15}$ [39]	–	–	228.0	98.0	–	–	4085.0	2.0
$Zr_{55}Ni_{25}Al_{20}$ [40]	–	–	226	92.7	1040	3.6	2662	3.7
$Fe_{48}Cr_{15}Mo_{14}C_{15}B_6Y_2$ [41]	–	–	166.6	78.1	363.3	21.0	2583.3	0.9
$Fe_{39}Co_9Cr_{15}Mo_{14}C_{15}B_6Y_2$ [41]	–	–	166.5	81.4	352.3	18.0	2230.7	0.6

Pure metal	$\tau_{defect\text{-}free}$ (ps)	$\tau_{monovacancy}$ (ps)
Ce [42]	197	315
Ga [42]	165	238
Cu [42]	105	178
Fe [42]	101	181
Ni [42]	96	169
Zr [42]	156	269

$Ce_{70}Ga_xCu_{30-x}$ ($x = 6$–13; at.%) BMGs [26]. $Ce_{70}Ga_xCu_{30-x}$ BMGs exhibit excellent GFA with strong composition-dependence in a wide composition range of $4 \le x \le 15$, which is rarely observed experimentally in a multicomponent system [26]. It was found that the Ce-concentrated packing state higher than that of Ce crystal appears at ambient pressure and this anomalous packing state sensitively varied with GFA. Formation mechanism of BMGs with higher GFA will be discussed on the basis of the efficient cluster packing model [6,7,27] taking above-mentioned anomalous packing state into consideration.

2. Experimental procedures

Master alloy ingots with nominal atomic percent compositions of $Ce_{70}Ga_xCu_{30-x}$ ($6 \le x \le 13$) were prepared by arc-melting mixtures of commercial-purity Ce (97.5 wt%), high-purity Ga (99.9%), Cu (99.99%), Al (99.99%) and Nb (99.9%) metals in a purified argon atmosphere. The ingots were remelted more than four times and suction-cast into a Cu-mold to prepare a series of Ce-Ga-Cu bulk glassy rods with a diameter of 5 mm. The amorphous state of the as-cast samples was confirmed by X-ray diffraction (XRD) using a D/MAX2500V diffractometer with Cu $K\alpha$ radiation at 40 kV. Thermal properties of the samples were examined by differential scanning calorimetry (DSC) under a purified nitrogen atmosphere in a PE 8000 system. For positron annihilation experiments, the samples were cut into two identical disks with a thickness of 2 mm.

To reveal the bonding characters of Ce-Ga-Cu BMGs, the density of states (DOS) for $Ce_{70}Al_{10}Cu_{20}$ and $Ce_{70}Ga_{10}Cu_{20}$ at 850 K were calculated by first-principles calculations, the framework of density functional theory (DFT) was implemented in the Vienna ab initio simulation package (VASP) [28,29]. The energy cutoff of the electronic wave functions is 300 eV. The generalized gradient approximation (GGA) in form of Perdew-Burke-Ernzerhof (PBE) was adopted for exchange-correlation potential [30]. The initial structures were obtained by ab initio molecules dynamic (AIMD) simulations. In the AIMD simulations, the canonical ensemble (NVT) was adopted with a Nosé-Hoover thermostat [31]. The time step is 3 fs. A supercell containing 100 atoms (70Ce + 10Al + 20Cu or 70Ce + 10Ga + 20Cu) was used in our simulations. Because of the finite periodic boundary condition, a small supercell containing one hundred atoms may not describe the intermediate-range structural order of an amorphous structure very well, however, it can describe the short-rang structural order more accurately. We know that the 4f electrons of Ce are mainly influenced by the nearest-neighbor atoms, so the calculated local electronic structures based on the structure obtained from the simulation with a smaller supercell should be convincing. The simulations were performed at the Γ point alone, which was widely used in AIMD simulations. The initial structure at 2000 K was constructed randomly and it has relaxed for 6 ps? Then the temperature of the liquid alloys were gradually reduced to 850 K. The average cooling rates for the quenching process is about 6×10^{13} K/fs. Then the structures at 850 K were randomly picked out for DOS.

Positron annihilation lifetime and coincident Doppler broadening (CDB) spectroscopy were performed at room temperature. The positron source (^{22}Na), sealed in a thin foil of Kapton, was mounted in a sample-source-sample sandwich for the measurements. Positron lifetime spectra (~1×10^6 coincidence counts) were recorded with digital oscilloscope-based system, in which the time resolution of 190 ps full-width at half-maximum (FWHM) was