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Journal of Alloys and Compounds 434–435 (2007) 149–151

Journal of ALLOYS AND COMPOUNDS

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# Stability and electronic structure of Zr-based ternary metallic glasses and relevant compounds

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Available online 6 October 2006

**Abstract**

The electronic structure of the Zr-based metallic glasses has been investigated by theoretical and experimental approaches. One approach is band calculations of the $Zr_2Ni$ ($Zr_{66.7}Ni_{33.3}$) compound to investigate the electronic structure of the $Zr_{66.7}Ni_{33.3}$ metallic glass ($\Delta T_x = 0$ K) of which the local atomic structure is similar to that of the $Zr_2Ni$ compound. The other is photoemission spectroscopy of the $Zr_{50}Cu_{35}Al_{15}$ bulk metallic glass (BMG) ($\Delta T_x = 69$ K). Here $\Delta T_x = T_x - T_g$ where $T_x$ and $T_g$ are crystallization and glass transition temperature, respectively. Both results and previous ones on the $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG indicate that there is a pseudogap at the Fermi level in the electronic structure of these Zr-based metallic glasses, independent of the value of the $\Delta T_x$. This implies that the pseudogap at the Fermi level is one of the factors that stabilize the glass phase of Zr-based metallic glasses.


*Keywords:* Metallic glass; Relevant compound; Phase stability; Electronic structure; Band calculations; Pseudogap

## 1. Introduction

The phase stability of the metallic glass has been well discussed from the viewpoint of thermodynamics. For example, Giessen considered the phase stability of Zr-based and Ni-based metallic glasses using two parameters, i.e. mixing enthalpy $-\Delta H$ and ratio of atomic radii $r/R$ [1]. Thermodynamic considerations have been also taken over to discuss the stability of the bulk metallic glasses (BMG) [2]. Although such thermodynamic considerations provide a macroscopic outline to understand the phase stability, the interpretation based on the local atomic structure and electronic structure is indispensable in order to elucidate the intrinsic mechanism for their phase stability, especially the high stability of BMGs. In terms of the local atomic structure, many researchers have contributed to this field by applying various kinds of diffraction techniques including X-ray, neutron and TEM. We consider that to elucidate the electronic structure is most important to clarify the origin of the stability of metallic glasses, especially BMGs.

Soda et al. recently studied the electronic structure of $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG by photoelectron spectroscopy in order to understand the origins of its glass phase stability and unique mechanical properties from the microscopic point of view [3]. Valence-band photoelectron spectra showed three bands ascribed to the Zr 4d, Ni 3d and Cu 3d states. The important point concerned with the glass phase stability in their results was that the valence-band photoelectron spectrum showed clear dip around the Fermi level, i.e. the pseudogap due to the reduction of the Zr 4d band. In addition a high-resolution valence-band spectrum revealed intensity reduction at the Fermi level in the sp-bands, indicating that there is also a pseudogap at the Fermi level in the sp-bands. These pseudogaps at the Fermi level in the electronic structure may contribute to the glass formation of the $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG.

In this manuscript, we have investigated the electronic structure of the Zr-based metallic glasses using theoretical and experimental approaches. One approach is the band calculations of the $Zr_2Ni$ ($Zr_{66.7}Ni_{33.3}$) compound to investigate the electronic

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doi:10.1016/j.jallcom.2006.08.277

structure of the $Zr_{66.7}Ni_{33.3}$ metallic glass since Fukunaga et al. have recently pointed out that its local atomic structure is similar to that of the $Zr_2Ni$ compound [4]. The other is the photoemission spectroscopy of the $Zr_{50}Cu_{35}Al_{15}$ BMG. Here, the $Zr_{66.7}Ni_{33.3}$ metallic glass shows no glass transition, i.e. $\Delta T_x = 0$ K, and the $Zr_{50}Cu_{35}Al_{15}$ BMG has $\Delta T_x = 62$ K [5] and is smaller than that of the $Zr_{55}Cu_{30}Ni_5Al_{10}$ ($\Delta T_x = 88$ K) BMG reported previously [3].

## 2. Experimental procedure

Alloy ingots were prepared on the arc-melting furnace under purified argon atmosphere. Metallic glasses ribbon of $Zr_{66.7}Ni_{33.3}$ was prepared by conventional single-roll melt spinning in purified argon atmosphere. Bulk metallic glasses of $Zr_{50}Cu_{35}Al_{15}$ were prepared by a conventional casting using a copper mold in purified argon atmosphere. The glassy nature was identified by X-ray diffraction using monochromatized Cu Kα radiation. Thermal stability was investigated by the differential scanning calorimetry (DSC) in a flow of purified argon atmosphere. The heating rate during DSC measurements was about 0.67 K/s.

The electronic band calculations for the $Zr_2Ni$ compound were performed by the linear muffin-tin orbital—atomic sphere approximation (LMTO-ASA) method. $Zr_2Ni$ compound is of the $Al_2Cu$-type *tI*12 structure. The space group of the structure is *I4/mcm*. The atomic positions of Zr and Ni were Zr: 4a 0.1629, 0.6629, 0 and Ni: 8h 0, 0, 1/4 [6]. The cell parameters were $a = 6.477$ Å and $c = 5.241$ Å [6]. Photoelectron spectra were recorded under ultrahigh vacuum of $2.4 \times 10^{-8}$ Pa at 25 K. Total energy resolution including the thermal broadening was set to 0.04–0.13 eV at the photon energy $h\nu$ of 20–90 eV with the use of the synchrotron light from UVSOR-II and set to 0.008 eV for the high-resolution measurement, confirmed by measuring the Fermi edge in the photoelectron spectra of an evaporated Au film. The origin of the binding energy $E_B$, i.e. the Fermi energy, was also determined by the Fermi edge of the Au film. Clean surfaces for the photoelectron measurement were obtained by in situ scraping the specimens with a diamond file.

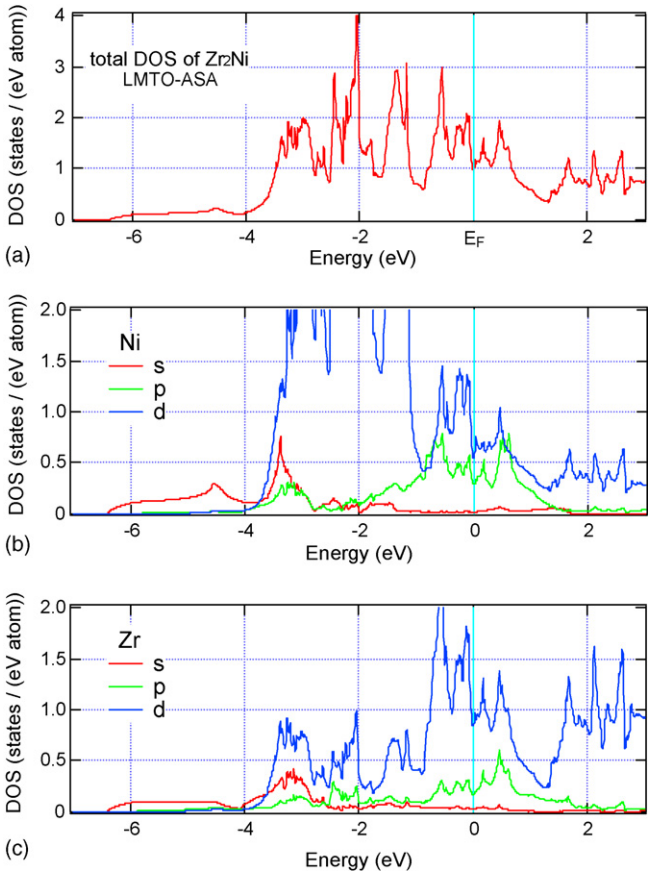


Fig. 1. The result of the band calculations of the $Zr_2Ni$ compound. (a) Total density of states (DOS), (b) partial DOS: Zr, and (c) partial DOS: Ni.

## 3. Results and discussion

Fig. 1 shows the result of the band calculations of the $Zr_2Ni$ compound. It is found that the Zr 4d-band mainly contributes to the density of states at the Fermi level. There is a clear deep pseudogap at the Fermi level located almost at the bottom of the pseudogap. As mentioned in the introduction, the $Zr_{66.7}Ni_{33.3}$ metallic glass has almost the same local structure as the $Zr_2Ni$ ($Zr_{66.7}Ni_{33.3}$) compound. Therefore, the $Zr_{66.7}Ni_{33.3}$ metallic glass is expected to have almost the same electronic structure although it may be a blurred because of the non-periodicity of the glassy structure. This indicates that there is also a pseudogap at the Fermi level in the electronic structure of the $Zr_{66.7}Ni_{33.3}$ metallic glass as well as the $Zr_2Ni$ compound and implies that the pseudogap at the Fermi level in the electronic structure is one of the factors to stabilize the glassy state of the $Zr_{66.7}Ni_{33.3}$ metallic glass. The partial density of states of the $Zr_2Ni$ compound shows that both Zr and Ni contribute to the formation of the pseudogap at the Fermi level. It should be noted that there is a pseudogap in the sp bands as well as the d-band. The Fermi level is also located at the bottom of the sp-bands pseudogap. These results indicate that the sp-bands of the $Zr_2Ni$ compound also contribute the formation of the pseudogap. Although the sp-bands structure of the $Zr_{66.7}Ni_{33.3}$ metallic glass may be blurred compared to that of the $Zr_2Ni$ compound, the intrinsic characteristic of the electronic structure may be the same.

Fig. 2(a) shows the photoemission spectrum of the $Zr_{50}Cu_{35}Al_{15}$ BMG. It is found that there is a peak below the Fermi level which is attributable to the Zr 4d band. The intensity of the photoemission spectrum decreases toward the Fermi level, indicating that there is a pseudogap at the Fermi level. Fig. 2(b) shows the high-resolution spectrum recorded at 25 K with a He I light source ($h\nu = 17.5$ eV) for the valence-bands near the Fermi level of the $Zr_{50}Cu_{35}Al_{15}$ BMG. The spectrum of the reference Au is also shown in the figure. The intensity for the metallic glass decreases below the 0.092 eV binding energy. Zr 4d states are peaked at the binding energy 0.3–0.6 eV and its ionization cross section decreased at $h\nu = 21.2$ eV [3]. This implies that the Zr 4d-band does not contribute so much to the spectral profiles near the Fermi level at this photon energy. The intensity reduction below the 0.092 eV binding energy indicates that the small pseudogap is also formed at the Fermi level in the sp bands as for $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG reported previously [3]. As mentioned in the introduction, the $Zr_{66.7}Ni_{33.3}$ metallic glass, the $Zr_{50}Cu_{35}Al_{15}$ BMG and the $Zr_{55}Cu_{30}Ni_5Al_{10}$ ($\Delta T_x = 88$ K) metallic glass have $\Delta T_x = 0$ K, $\Delta T_x = 62$ K and $\Delta T_x = 88$ K, respectively. The theoretical and experimental results in this and previous studies indicate that there is a pseudogap at the Fermi level in the total and sp-bands electronic structure of these three metallic glasses, independent of the value of the $\Delta T_x$.

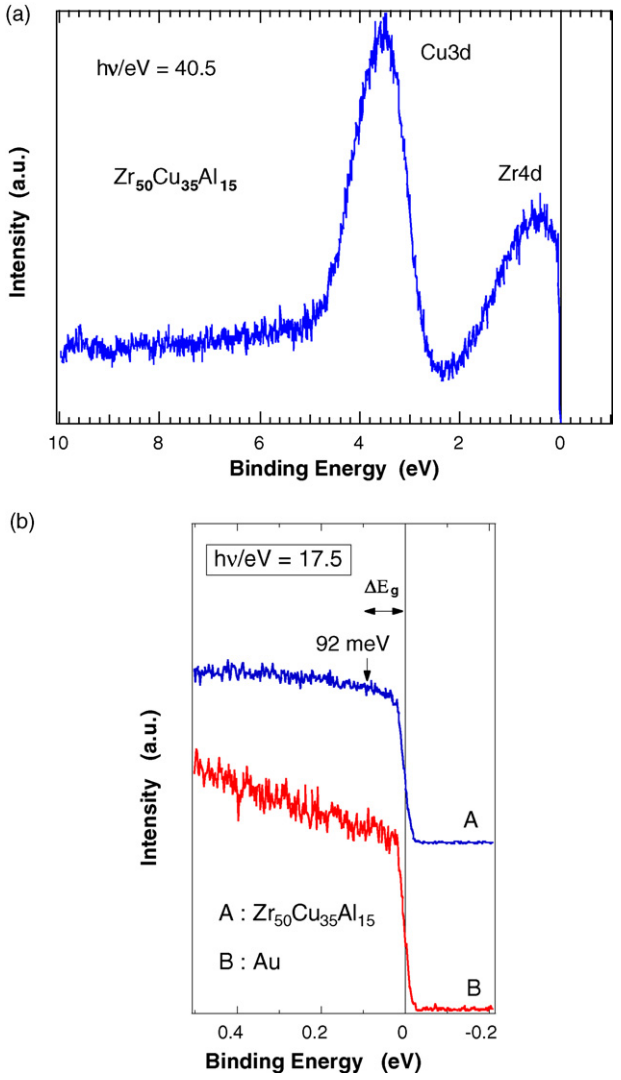


Fig. 2. (a) Valence-band photoelectron spectra of $Zr_{50}Cu_{35}Al_{15}$ BMG. (b) Detailed valence band spectra near the Fermi level of the $Zr_{50}Cu_{35}Al_{15}$ BMG and Au as a reference.

## 4. Conclusion

The electronic structures of $Zr_{66.7}Ni_{33.3}$ ($\Delta T_x = 0$ K) and $Zr_{50}Cu_{35}Al_{15}$ ($\Delta T_x = 69$ K) metallic glasses have been investigated theoretically and experimentally. Band calculations for $Zr_2Ni$ compound with local atomic structure similar to that of the $Zr_{66.7}Ni_{33.3}$ metallic glass has been performed. The photoemission spectrum of the $Zr_{50}Cu_{35}Al_{15}$ BMG has been also measured. Both results and previous study on the $Zr_{55}Cu_{30}Ni_5Al_{10}$ BMG ($\Delta T_x = 88$ K) indicate that there is a pseudogap at the Fermi level in the electronic structure of these metallic glasses, independent of the value of the $\Delta T_x$.

## Acknowledgements

The authors are grateful to S. Kimura and T. Ito for their helps on the UPS measurements. This research was supported by the Ministry of Education, Culture, Sports, Science and Technology, Grant-in-Aid for Scientific Research on Priority Areas.

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