Anomalous temperature dependent elastic moduli of Ce-based bulk metallic glass at low temperatures

P. Yu, R. J. Wang, D. Q. Zhao, and H. Y. Bai[a)]
Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

(Received 27 September 2007; accepted 26 October 2007; published online 14 November 2007)

We report the abnormal temperature dependent elastic moduli of Ce-based bulk metallic glass (BMG) at low temperatures. Unlike other BMGs with stiffness mode, the Ce-based metallic glass exhibits an anomalous softening longitudinal acoustic mode with the decrease of temperature. Particularly, the bulk modulus shows a continuous decrease upon cooling indicating the softening of the BMG, which is completely different from that of other metallic glasses and conventional alloys. The physical origin of this abnormal elastic behavior is attributed to the alterative valences and electronic configurations at low temperatures. © *2007 American Institute of Physics*.
[DOI: 10.1063/1.2813639]

Cerium-based bulk metallic glasses (BMGs) have attracted great attention due to their unique properties since they were developed.[1–4] They have excellent glass-forming ability, small elastic moduli, and an exceptionally low glass transition temperature T_g similar to or lower than that of many polymers. These features make them become a model system for the study of glass transition, plastic molding, slow dynamics and glass-forming mechanism in the glassy alloys. Through the measurement of the elastic moduli under different conditions, one can obtain important information on structural and vibrational characteristics of the materials.[5] The elastic moduli of Ce-based BMGs under high pressure have been studied and compared to those of other BMG materials.[6] The interesting result is that the Ce-based BMG, unlike other BMGs with normal mode stiffening, exhibits an anomalous softening longitudinal acoustic mode under pressure.[6] This anomalous behavior is attributed to the intrinsic features of the Ce element and the unique structure of the Ce-based BMG. Cryogenic condition is another powerful thermodynamic technique to explore the physical mechanism and structure of a material. The observation of elastic behavior by acoustic measurement at low temperatures down to the liquid nitrogen temperature can reveal the temperature influence on mechanical properties.[7,8]

In this work, the cryogenic and acoustic experiments are performed on a $Ce_{68}Al_{10}Cu_{20}Co_2$ BMG. Meanwhile, a $La_{68}Al_{10}Cu_{20}Co_2$ BMG is studied under the same conditions for comparison. La has similar valences and ionic radii to Ce, but without $4f$ electrons, the corresponding $La_{68}Al_{10}Cu_{20}Co_2$ BMGs was used as a reference for the contrast of $4f$ electron contribution to the elastic properties. The velocities of ultrasonic waves have been measured *in situ* for the BMGs as the functions of temperature. The unusual response of the acoustic and elastic properties of the Ce-based BMG is found and contrasts to the La-based and other BMGs. The possible mechanism of the abnormal behavior is discussed.

The $Ce_{68}Al_{10}Cu_{20}Co_2$ and $La_{68}Al_{10}Cu_{20}Co_2$ 5 mm in diameter and 50 mm long were prepared by suction casting the molten master alloy into water-cooling copper mold.[1,5,6] The BMG rods were cutted into cylinders with a length of about 7 mm and their ends were polished flat and parallel. The acoustic velocities of the BMGs were measured from the liquid nitrogen temperature to 300 K by using a pulse echo overlap method. The travel time of ultrasonic waves propagating through the rod with a 10 MHz carry frequency was measured by a MATEC 6600 ultrasonic system. The measuring sensitivity was of the order of 0.5 ns. The mass density was measured by the Archimedean technique and the accuracy lies within 0.1%. Elastic constants (e.g., Young's modulus E, shear modulus G, bulk modulus B, and Poisson's ratio ν) were derived from the acoustic velocities and the densities.

Figure 1 shows the differential scanning calorimetry (DSC) curves taken at a heating rate of 20 K/min for the $Ce_{68}Al_{10}Cu_{20}Co_2$ and $La_{68}Al_{10}Cu_{20}Co_2$ BMGs. A distinct glass transition and obvious crystallizations shown in the DSC curves further confirm the truly glassy structure of the two alloys. The two DSC curves display similar endothermal and exothermal processes except for the different glass transition temperatures and crystallization temperatures. It is notable that the two samples have very low glass transition temperatures. The similar compositions and thermodynamic behaviors are of benefit to the comparison of the acoustic and the elastic properties between the two alloys.

The mass densities ρ, the longitudinal and transverse acoustic velocities V_L and V_T at room temperature, and the elastic moduli for the two BMGs are listed in Table I. These values compare well with those reported earlier for BMGs.[6,9]

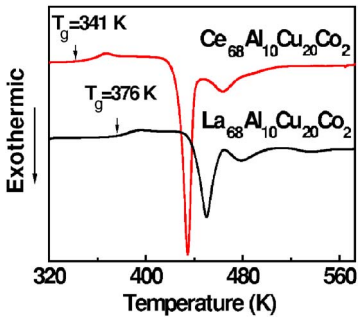

FIG. 1. (Color online) The DSC curves for the $Ce_{68}Al_{10}Cu_{20}Co_2$ and $La_{68}Al_{10}Cu_{20}Co_2$ BMGs.

[a)]Author to whom correspondence should be addressed. Electronic mail: hybai@aphy.iphy.ac.cn

TABLE I. The density ρ, ultrasonic velocities V_L and V_T, the elastic constants E, G, B, and ν for the $La_{68}Al_{10}Cu_{20}Co_2$ and $Ce_{68}Al_{10}Cu_{20}Co_2$ BMGs at ambient temperature.

Samples	ρ (g/cm^3)	V_L (km/s)	V_T (km/s)	E (GPa)	G (GPa)	B (GPa)	ν
$La_{68}Al_{10}Cu_{20}Co_2$	6.152	2.911	1.379	31.7	11.7	36.6	0.355
$Ce_{68}Al_{10}Cu_{20}Co_2$	6.752	2.612	1.322	31.4	11.8	30.3	0.328

The temperature dependences of V_L and V_T of the two BMGs are shown in Figs. 2(a) and 2(b). For $La_{68}Al_{10}Cu_{20}Co_2$, both V_L and V_T increase roughly in linear with the decreasing temperature, which is well consistent with the measured results reported earlier for other BMGs.[9] The results indicate that both transverse and longitudinal acoustic phonons are continuously stiffening under cooling. However, for the $Ce_{68}Al_{10}Cu_{20}Co_2$, V_L and V_T show very different behaviors with the decreasing temperature. Their dependences on temperature completely deviate from the linear relationship. Furthermore, the V_L exhibits positive temperature coefficient which indicates the mode softening under cooling and is contrary to the regularity of La-based and other BMGs. This result reveals that the Ce-based BMG has different temperature effects compared to other metallic glasses and conventional alloys.[9–11]

The variations of the E, G, B, and ν of the two BMGs are shown in Figs. 3(a) and 3(b) as functions of temperature, respectively. The E, G, and B of the $La_{68}Al_{10}Cu_{20}Co_2$ monotonously increase with the decreasing temperature, indicating the continuous stiffening of BMGs.[12] However, for the $Ce_{68}Al_{10}Cu_{20}Co_2$, although E and G display stiffening mode with decreasing temperature, B abnormally decreases with decreasing temperature. The decrease of bulk modulus directly indicates the softening of Ce-based BMG under cooling. Moreover, E, G, and B all completely deviate from the quasilinear tendency in the measured temperature range. In contrast to La-based and other BMGs, the bulk modulus and Poisson's ratio of the Ce-based BMG have the larger variations upon decreasing temperature.[9,11] These results show that the elastic moduli of Ce-based BMG are easily influenced by temperature. The ν of the two BMGs monotonously decreases under cooling indicating that there is a stiffening of transverse acoustic phonons in the BMGs.[9]

As a major component of the Ce-based BMG, Ce plays a key role in its physical behavior and determines its properties. For the Ce element, because the energy levels of the inner $4f$ electrons are very closed to those of the outer or valence $5d$ and $6s$ levels, only small amounts of energy are necessary to change the relative occupancy of these electronic levels giving rise to a variable electronic structure.[13] The valence of Ce can be changed driven by the low temperature and/or high pressure. Experimentally, when temperature is below 273 K, Ce is unstable and begins to transform incompletely to another electronic configuration.[13,14] Under 100 K, the valence of Ce becomes a nonintegral valence 3.67 from the valence 3 at room temperature, which corresponds to the lattice collapse arising from the change in electronic structure.[14,15] The mutable electronic structure leads to a complex phase diagram and the well known solid-solid isostructural $\gamma \leftrightarrow \alpha$ phase transition.[13–15] For the Ce-based BMG, the abnormal elastic moduli are closely related to the evolution of Ce's electronic configuration at low temperatures. The softening of longitudinal acoustic phonons and the sharp drop of bulk modulus correspond to the relaxed structure and the shrinkage of atomic radius owing to the continuous increased valence of Ce upon cooling. Without the $4f$ electrons and changeful electronic structure, La-based BMG displays a normal acoustic and elastic behavior under cooling, which just implies the abnormal elastic

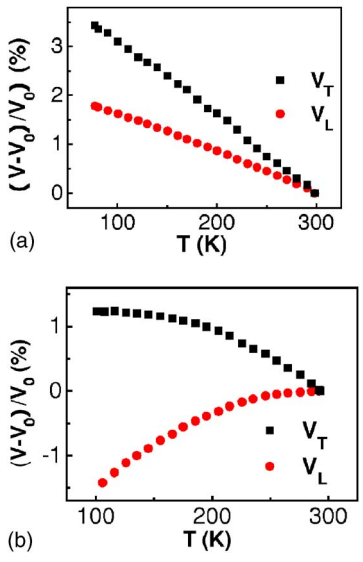

FIG. 2. (Color online) The temperature dependences of V_L and V_T of the $La_{68}Al_{10}Cu_{20}Co_2$ (a) and $Ce_{68}Al_{10}Cu_{20}Co_2$ (b) BMGs; V_0 is the velocity at ambient temperature.

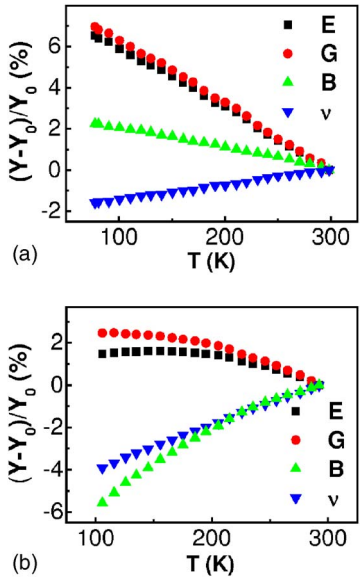

FIG. 3. (Color online) The dependences of E, G, B, and ν of the $La_{68}Al_{10}Cu_{20}Co_2$ (a) and $Ce_{68}Al_{10}Cu_{20}Co_2$ (b) BMGs on temperature. The Y_0 is the modulus at ambient temperature.

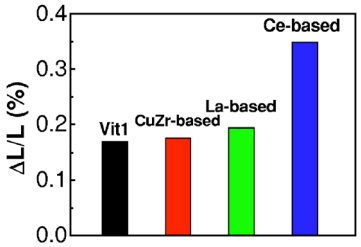

FIG. 4. (Color online) The comparison for the relative length changes $\Delta L/L_0=(L_0-L_{\mathrm{LN}})/L_0$ between the state (L_{LN}) of liquid nitrogen temperature and the ambient state (L_0) for the Vit1, CuZr-based, La-based, and Ce-based BMGs.

moduli of Ce-based BMG root in the alterative electronic configuration of Ce.

To clarify the volume shrinkage, we test the variation of length of the Ce-based sample upon cooling down to the liquid nitrogen temperature and compare to the other representative BMGs. Figure 4 shows the comparison for the relative length changes $\Delta L/L_0=(L_0-L_{\mathrm{LN}})/L_0$ between the state (L_{LN}) at the liquid nitrogen temperature and the ambient state (L_0) for the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ (Vit1), $(Cu_{50}Zr_{50})_{95}AL_5$, $La_{68}Al_{10}Cu_{20}Co_2$, and $Ce_{68}Al_{10}Cu_{20}Co_2$ BMGs. The obtained average linear expansion factor from room temperature to liquid nitrogen temperature are 7.81×10^{-6}, 8.08×10^{-6}, 8.91×10^{-6}, and 15.98×10^{-6} K^{-1} for Vit1, CuZr-based, La-based, and Ce-based BMGs, respectively. It is remarkable that the Ce-based BMG exhibits a larger contraction compared to the other three BMGs under cooling. This larger contraction upon decreasing temperature indicates the intensive reduction of interatomic distance.[16] The magnitude of contraction in the Ce-based BMG is about two times of that in other BMGs. The result indicates, except for the normal cooling shrinkage, the shrinkage of atomic radius from the increasing valence that occurs obviously. The above results imply an electronic phase transition in the Ce-based alloys, most likely a second-order amorphous-to-amorphous phase transition that is intensely studied by recent researches.[17–20] Our experimental results supply a circumstantial evidence to prove the phase transition in Ce-based metallic glasses.

In summary, through the comparison with the similar La-based and other metallic glassy materials, we found that the soft longitudinal acoustic mode and softening bulk modulus under cooling are the unique properties of Ce-based BMG. The origin of this abnormal behavior is attributed to the alterative valences and electronic configurations of Ce under cooling. The results potentially imply a second-order amorphous-to-amorphous phase transition in Ce-based metallic glass.

We are grateful to W. H. Wang and J. Q. Wang for discussions. The financial support of the NSF of China (50671117 and 50621061) is appreciated.

[1] B. Zhang, D. Q. Zhao, M. X. Pan, W. H. Wang, and A. L. Greer, Phys. Rev. Lett. **94**, 205502 (2005); Nature (London) **435**, 717 (2005).
[2] Z. Bian and A. Inoue, Mater. Trans. **47**, 2599 (2006).
[3] W. H. Li, K. Shin, B. C. Wei, and T. H. Zhang, Appl. Phys. Lett. **90**, 171928 (2007).
[4] X. K. Xi, B. Zhang, W. H. Wang, and Y. Wu, Phys. Rev. Lett. **99**, 095501 (2007).
[5] W. H. Wang, J. Appl. Phys. **99**, 093506 (2006); W. H. Wang, Prog. Mater. Sci. **52**, 540 (2007); W. H. Wang, C. Dong, and C. H. Shek, Mater. Sci. Eng., R. **44**, 45 (2004).
[6] B. Zhang, R. J. Wang, and W. H. Wang, Phys. Rev. B **72**, 104205 (2005).
[7] S. Takeuchi, T. Hashimoto, A. P. Tsai, and A. Inoue, Mater. Trans., JIM **41**, 1443 (2000).
[8] H. Q. Li, C. Fan, K. X. Tao, H. Choo, and P. K. Liaw, Adv. Mater. (Weinheim, Ger.) **18**, 752 (2006).
[9] P. Yu, R. J. Wang, D. Q. Zhao, and H. Y. Bai, Appl. Phys. Lett. **90**, 251904 (2007).
[10] F. Augereau, D. Laux, L. Allais, M. Mottot, and C. Caes, Ultrasonics **46**, 34 (2007).
[11] Z. Y. Zhang, V. Keppens, P. K. Liaw, and A. Inoue, J. Mater. Res. **22**, 364 (2007).
[12] K. Tanaka, T. Ichitsubo, and E. Matsubara, Mater. Sci. Eng., A **442**, 278 (2006).
[13] D. C. Koskenmaki and K. A. Gschneidner, Jr., *Handbook on the Physics and Chemistry of Rare Eearths* (North-Holland, Amsterdam, 1978), Vol 1, p. 337.
[14] J. M. Lawrence, P. S. Riseborough, and R. D. Rarks, Rep. Prog. Phys. **44**, 1 (1981).
[15] S. Bustingorry, E. A. Jagla, and J. Lorenzana, Acta Mater. **53**, 5183 (2005).
[16] A. K. Mcmahan, C. Huscrosft, R. T. Scalettar, and E. L. Pollock, J. Comput.-Aided Mater. Des. **5**, 131 (1998).
[17] H. W. Sheng, H. Z. Liu, Y. Q. Cheng, J. Wen, P. L. Lee, W. K. Luo, S. D. Shastri, and E. Ma, Nat. Mater. **6**, 192 (2007); A. R. Yavari, *ibid.* **6**, 181 (2007).
[18] M. B. Tang, H. Y. Bai, W. H. Wang, D. Bogdanov, K. Winzer, K. Samwer, and T. Egami, Phys. Rev. B **75**, 172201 (2007).
[19] Q. S. Zeng, Y. C. Li, and J. Z. Jiang, Proc. Natl. Acad. Sci. U.S.A. **104**, 13565 (2007).
[20] B. Zhang, H. Y. Bai, Y. Wu, and W. H. Wang, Phys. Rev. B **76**, 012201 (2007).