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Low temperature specific heat and thermal conductivity of bulk metallic glass $(Cu_{50}Zr_{50})_{94}Al_6$

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ABSTRACT

The low temperature specific heat and thermal conductivity of $(Cu_{50}Zr_{50})_{94}Al_6$ bulk metallic glass have been studied experimentally. A low temperature anomaly in the specific heat is observed in this alloy. It is also found that in addition to Debye oscillators, the localized vibration modes whose vibration density of state has a Gaussian distribution should be considered to explain the low temperature phonon specific heat anomaly. The phonon thermal conductivity dependence on temperature for the sample does not show apparent plateau characteristics as other glass materials do; however, the influence of the resonant scattering from the localized modes on the lattice thermal conductivity is prominent in the bulk metallic glass at low temperatures.

In the past two decades, bulk metallic glasses (BMGs) have attracted considerable attention both in fundamental research and engineering due to their many unique properties, such as excellent corrosion resistance, remarkably high strength and hardness, and large elastic deformation limit [1,2]. Since the BMGs have simple atomic glassy structure and dense random packing with strong interaction among their components, the intramolecular, reorientational and translation motions of molecules, observed in nonmetallic glasses such as polymeric and ceramic glasses, do not appear in these glasses. The BMGs may be good systems for investigating the low temperature physical property anomalies in glasses [3–9]. The low temperature specific heats of CuZr-based BMGs have been investigated by Wang and his co-workers [8,10–12]: they found that the Debye model alone does not quantitatively explain the lattice contribution to the specific heat. They proposed that an Einstein oscillator should be considered to account for the low temperature specific heat anomalies in the CuZr-based BMGs. However, the origin of the anomalies is still a debated issue and the nature of the anomalies needs further exploration. On the other hand, the thermal conductivity of phonons is proportional to the product of the specific heat and the mean free path of the phonons. The thermal conductivity anomaly at low temperatures has also been observed in noncrystalline dielectric solids [6,13], as well as in BMGs [9,14]. To give comprehensive information on phonons in BMGs at low temperatures, we have measured the low temperature specific heat and thermal conductivity of a representative bulk metallic glass $(Cu_{50}Zr_{50})_{94}Al_6$. We have also measured the resistivity of the sample from 55 down to 2 K to subtract the electron contributions to the thermal conductivity. We report the systematic studies of both the specific heat and thermal transport properties of this BMG in the following discussions.

The ingot of $(Cu_{50}Zr_{50})_{94}Al_6$ was prepared by a standard arc melting method under argon atmosphere. Stoichiometric amounts of the metal elements Cu (99.999%), Zr (99.995%) and Al (99.999%) were arc melted seven times. The BMG cylinder rod, 5 mm in diameter, was obtained by means of copper mold suction casting. The amorphous nature of the as-prepared sample was verified by X-ray diffraction, and further confirmed by differential scanning calorimetry (DSC). The DSC trace (Fig. 1) showed an endothermic event characteristic of a glass transition at $T_g = 701.6$ K, followed by one exothermic event characteristic of a crystallization process at $T_x = 763$ K. The specific heat measurement was carried out with the heat capacity option of a physical properties measurement system (PPMS-6000, Quantum Design). The relative error of the specific heat measurement is less than 2%. The thermal conductivity was measured by a four-probe leads configuration

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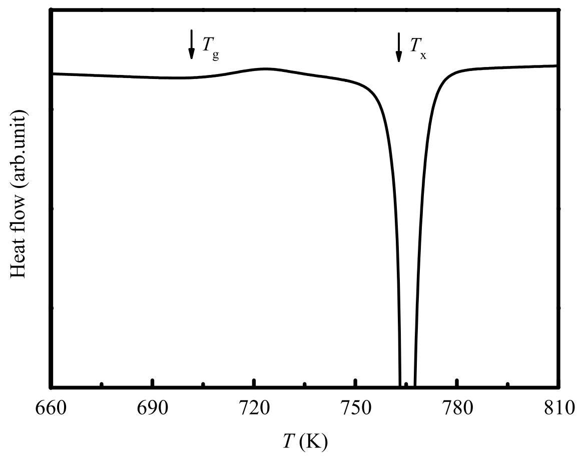

Fig. 1. DSC trace of $(Cu_{50}Zr_{50})_{94}Al_6$ BMG with a heating rate of 10 K/min. The glass transition temperature T_g and the crystallization temperature T_x are indicated by arrows.

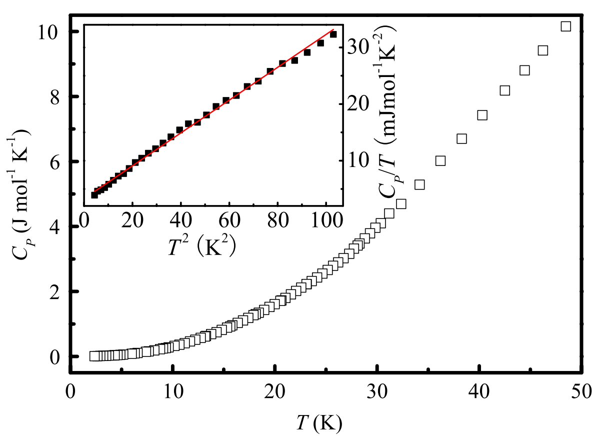

Fig. 2. (color online) Specific heat of $(Cu_{50}Zr_{50})_{94}Al_6$ BMG in the temperature range from 2 K to 50 K. Inset: the specific heat shown as C_P/T versus T^2; the solid line is the least-squares fitting result using the expression $C_p/T = \gamma + \beta T^2$ between 2 and 8 K.

method, in which two calibrated Cernox 1050 thermometers are used to measure the temperature of the hot and cold probes, respectively. The pressure of the sample chamber is less than 5×10^{-4} Torr during the specific heat and thermal conductivity measurements. The resistivity measurement was also performed in the PPMS with the standard four-probe method.

Fig. 2 shows the temperature dependence of the specific heat of $(Cu_{50}Zr_{50})_{94}Al_6$ from 2 to 50 K. To obtain the specific heat of the phonons, we need to determine the electronic contribution to the specific heat correctly. The inset of Fig. 2 presents a C_P/T versus T^2 plot below 8 K. We fitted the experimental data using the expression $C_p/T = \gamma + \beta T^2$, and the fitted results gave $\gamma = 3.3$ mJ mol^{-1} K^{-2} and $\beta = 0.29$ mJ mol^{-1} K^{-4}, respectively. Fig. 3 shows the C_{ph}/T^3 variation with temperature from 2 to 50 K. Subtracting the electronic contribution to the specific heat, one can clearly see that the specific heat of the phonons apparently deviates from the prediction of the Debye model and a bump centered around 6 K appears. This is the so-called boson peak [15–17], which is often observed in many nonmetallic glasses and defined as an excess with respect to the Debye contribution in the low frequency vibrational density of state (VDOS).

It is reported that an additional quantized Einstein oscillator should be considered to explain the low temperature anomaly of phonon specific heat [10,11,14,18,19]. Thus we fit the phonon specific heat data using the expression

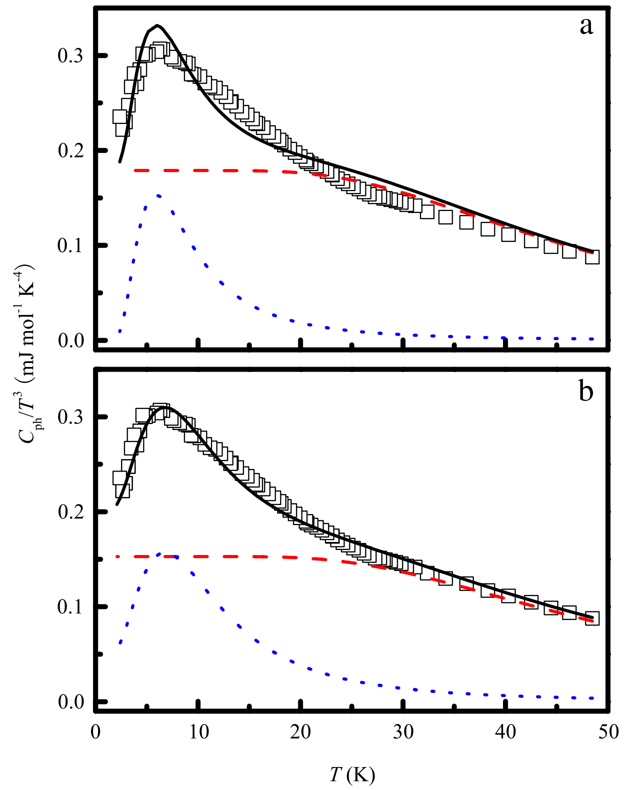

Fig. 3. (color online) The phonon specific heat of $(Cu_{50}Zr_{50})_{94}Al_6$ BMG plotted as C_{ph}/T^3 versus T (square symbols) along with (a) least-squares fit to Eq. (1) (solid line), and (b) least-squares fit to Eq. (2) (solid line). The dashed lines and dotted lines are the contributions of the Debye term and the Einstein term, respectively.

$$C_{ph} = n_D \cdot 9R(T/\theta_D)^3 \int_0^{\theta_D/T} \frac{\xi^4 e^{\xi}}{(e^{\xi}-1)^2} d\xi + n_E \cdot 3R(\theta_E/T)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2}, \quad (1)$$

where R is the gas constant, θ_D the Debye temperature, θ_E the Einstein temperature, $\xi = \hbar\omega/k_B T$ is a dimensionless quantity, and n_D and n_E are Debye-type and Einstein-type vibration strength per mole ($n_D + n_E = 1$), respectively. The solid line in Fig. 3(a) represents the least-squares fit to Eq. (1) with $\theta_D = 221$ K, $n_D = 0.993$, $\theta_E = 29$ K, and $n_E = 0.07$. The Debye temperature of $(Cu_{50}Zr_{50})_{94}Al_6$ BMG obtained from the least-squares fit to Eq. (1) is comparable to that of 275 K for $(Cu_{50}Zr_{50})_{96}Al_4$ BMG deduced from acoustic velocity measurements [8], which indicates the validity of the fitting process. From Fig. 3(a), one can see that the phonon specific heat can be well described by Eq. (1) below 5 K, while it significantly deviates from the prediction of Eq. (1) at higher temperatures.

The idea that an Einstein oscillator is used to explain the specific heat of BMG is based on the picture that there exist localized harmonic vibration modes in the glasses [10,13]. It is assumed that there is only one localized mode contribution to the VDOS in Eq. (1), which may be not the case in the glasses. Recently, it was found that two Einstein modes are necessary to be considered besides the Debye contribution to explain the low temperature heat capacity of $Cu_{6.198}Zn_{28.04}Al_{9.98}$ shape-memory alloy [20]. As for our sample, we suppose the localized vibration mode's contribution to the VDOS has a Gaussian distribution; then the phonon specific heat can be written as

$$C_{ph} = n_D \cdot 9R(T/\theta_D)^3 \int_0^{\theta_D/T} \frac{\xi^4 e^{\xi}}{(e^{\xi}-1)^2} d\xi$$