Tunneling states and localized mode in binary bulk metallic glass

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The low-temperature specific heat of $Cu_{50}Zr_{50}$ binary bulk metallic glass is systemically measured from 1.8 K to 50.5 K. The obvious effect of the tunneling states is determined at several Kelvin by both specific heat and electrical resistivity. The density of the electron-assisted tunneling states in the bulk metallic glass at several Kelvin exceed the typical value in insulating glasses below 1 K by 2–3 orders of magnitude, and the entropy of the tunneling states is about 7.85 mJ/mol K. The specific heat in the wide temperature range was analyzed by the conventional Debye and Einstein models, and the results demonstrate the existence of the localized mode which is correlated to the boson peak in the metallic glass.

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At low temperature, glasses exhibit a variety of interesting thermal, vibrational, and acoustic properties of considerable theoretical and experimental interest, which are different from those of crystalline solids. The specific heat of glasses is directly related to its atomic structure, or its vibrational and configurational entropy which is significantly affected by the nearest-neighbor configuration. At low temperature, typically $T<1$ K, the specific heat C_p of glasses depends approximately linear on temperature.[1] This is due to the existence of low-energy excitations which are commonly interpreted as a two-level system arising from tunneling of atoms or groups of atoms between two nearly degenerate local energy minima.[2,3] At $T>1$ K, the specific heat still deviates from the expected T^3 dependence, presenting a broad maximum in C_p/T^3.[4] The universal feature is related to a difference or excess in the vibrational density of states over the crystalline Debye behavior, which is known as the boson peak in glasses. Usually, the soft potential model,[4,5] which postulates the coexistence in glasses of acoustic phonons with quasilocalized low-frequency (soft) modes, is used to explain the excess specific heat of glasses. Nevertheless, the specific nature of the low-frequency vibrations is still a matter of intense debate.

The tunneling states observed below 1 K for the most cases are studied widely and systemically especially in insulating glasses.[1,6] The situation in metallic glasses is not simple because of the electronic degrees of freedom. The specific heat of both electrons and tunneling states is linear T-dependent at low temperature; It is difficult to distinguish the contributions to specific heat between electrons and tunneling states and to determine the density of tunneling states in metallic glasses. Fortunately, there are some superconductive metallic glasses,[7,8] where the conduction electrons can be ignored and the tunneling states have been studied below the superconductive temperature in the metallic glasses.[7,9] However, the electron-assisted tunneling states in metallic glasses have not been experimentally studied before.

The ribbons of CuZr metallic glasses had been investigated extensively.[9,10] Some compositions of the CuZr glasses show superconductivity. The density of tunneling states below the superconductive temperature is close to the typical value in insulating glasses in the order of about $10^{16}/cm^3$,[9,11] corresponding to about 10^{-6} per atom. However, the tunneling states above the superconductive temperature are not studied. Furthermore, the previous work involved was mainly about the properties in the narrow temperature range (below 10 K). In this paper, the specific heat of a recently developed simple $Cu_{50}Zr_{50}$ binary bulk metallic glass (BMG) in a large temperature range (1.8–50.5 K) is systematically studied. Compared with insulating glasses, the electron-assisted tunneling states have much larger entropy and higher density in the metallic glass. The specific heat of the BMG can be fitted well in the wide temperature range by conventional Debye and Einstein models indicating the existence of the localized mode which is correlated to the boson peak in the simple BMG.

$Cu_{50}Zr_{50}$ binary BMG was chosen as a model system because it is a simple nonmagnetic BMG with excellent glass-forming ability.[12] The BMG specimen was prepared by arc melting the pure Cu and Zr elements and then produced by suction casting the melt into a copper mold under a pure argon atmosphere; the details of the synthesis were described in Ref. 12. The specific heat measurement of the BMG with mass of 38.98 mg was carried out with the heat capacity option of a commercial Physical Properties Measurement System (PPMS, Quantum Design Inc.). The relative error of the specific heat measurement is less than 2%. The electrical resistivity was measured as a function of temperature by the PPMS using a standard four-probe technique.

The measured C_p of the BMG from 1.8 K to 50.5 K is shown as C_p/T^3 vs T in Fig. 1(a). Figure 1(b) presents C_p/T vs T^2 plot in the temperature range of 1.8 K and 20.6 K. Usually, the soft potential model[4,5] is used to explain the specific heat of glasses below 10 K. However, there is no obvious hump in the C_p/T^3 vs T plot and the specific heat in the wide low temperature range can be well fitted by $C_p/T=\gamma+\beta T^2$ without higher powers of T as shown in Figs. 1(a) and 1(b).[5] The soft potential model fails to explain the results of the BMG in the wide temperature range.[13]

The tunneling states contribute weakly to specific heat near 10 K,[2,3,14] so we can determine the electrons' and phonons' contributions to specific heat near 10 K by the linear fitting $C_p/T=\gamma+\beta T^2$ [see Fig. 1(b)]. The values of γ and β, obtained from the fit, are 2.74 mJ/mol K^2, 128.7 μJ/mol K^4, respectively. Just like other BMGs,[13,15]

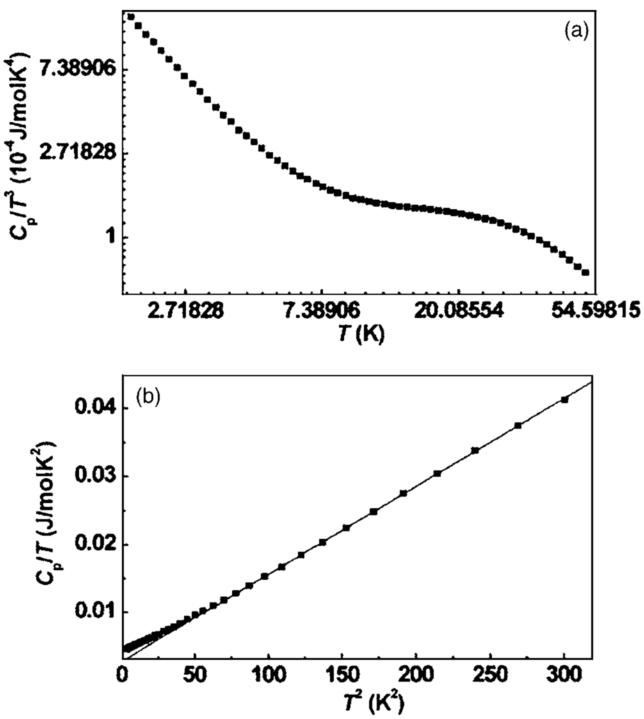

FIG. 1. The specific heat C_p of the $Cu_{50}Zr_{50}$ BMG in the temperature range from 1.8 K to 50.5 K. (a) The specific heat plotted as C_p/T^3 vs T. (b) The specific heat, shown as C_p/T vs T^2, the solid line is the results of the fitting specific heat using the expression: $C_p/T=\gamma+\beta T^2$.

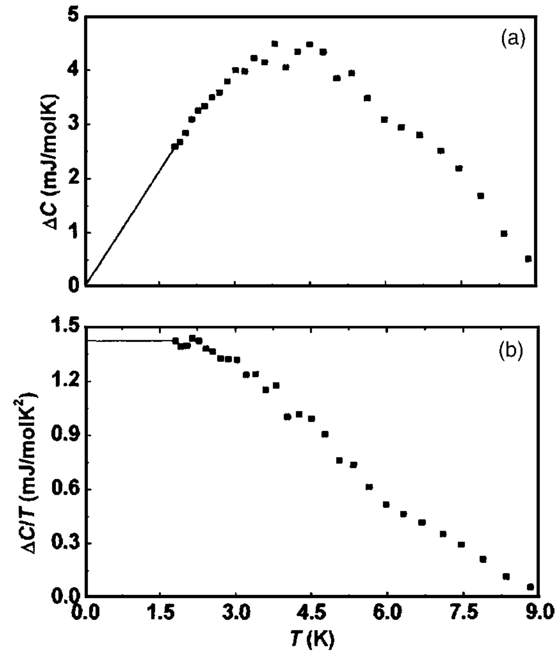

FIG. 2. The excess specific heat of the $Cu_{50}Zr_{50}$ BMG is shown as ΔC vs T in (a) and $\Delta C/T$ vs T in (b). The black lines are the extrapolated excess specific heat.

the data deviate from the linear in the lower temperature range, while the common phenomenon in BMGs has not been paid much attention before. In the nonmagnetic metallic glasses, the specific heat at low temperature mainly includes the contributions of the tunneling states, electrons and phonons. So after subtracting the electrons' and phonons' contributions which are determined around 10 K, the excess of the specific heat of the alloy ($\Delta C=C_p-\gamma T-\beta T^3$), which is shown in Fig. 2(a), should be the contribution of the tunneling states. The simple extrapolation in the glass is made by drawing straight lines from the lowest temperature data point to $T=0$, $C=0$ in Fig. 2(a) [these will be horizontal lines on the C/T plot in Fig. 2(b)]. A Schottky-type specific heat anomaly could be ascribed the specific heat excess, and its high-temperature tail should obey a T^2 dependence.[6] But like other metallic glasses,[15] the excess of the specific heat in Fig. 2(a) does not strictly follow the Schottky-type anomaly.

To further prove the deviation is due to the effect of the tunneling states at several Kelvin, the electrical resistivity of the BMG in the low temperature range was measured and shown in Fig. 3. The resistivity of the BMG shows negative temperature dependence. Below about 10 K, the resistivity in alloys should mainly be attributed to the residual resistivity and be close to a constant. However, the resistivity for the BMG increases slowly with decreasing temperature below about 13 K, and the T-dependent resistivity can be well explained by the Kondo-type model[16]

$$\rho(T)=\rho_0+A\cdot\rho_N(T)-\lambda\cdot\ln(T^2+\Delta^2), \qquad (1)$$

where ρ_0, A, λ, and Δ are constants, $\rho_N(T)$ is the regular electron-phonon term which is also close to zero at low temperature. The fitting result is shown in Fig. 3. The resistivity of the BMG above 15 K obviously, deviates from the Kondo-type model. The atoms (or clusters of atoms) in the BMG maybe in tunneling states between two sides of a double potential well, and the tunneling states affect the resistivity of the BMG.[16] The analysis of the resistivity reveals that there is the obvious effect of the tunneling states in the BMG at about several Kelvin.

The entropy of the tunneling states can be calculated by $\Delta S=\int_0^{T_{\max}}(\Delta C/T)dT$, and the value is 7.85 mJ/mol K for the BMG. Because the problem of the tunneling states is in anal-

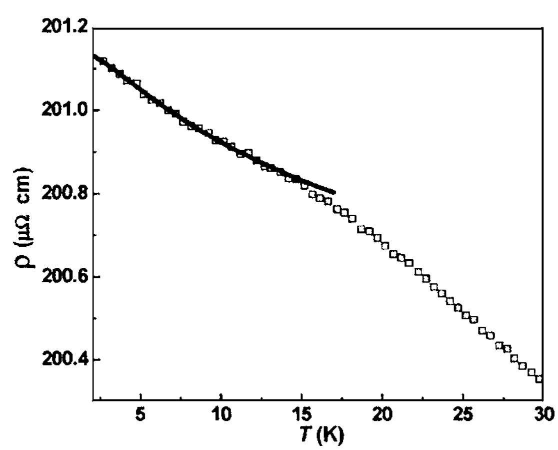

FIG. 3. The electrical resistivity of the $Cu_{50}Zr_{50}$ BMG above 2 K. The line is the least-squares fitting result by the Kondo model.

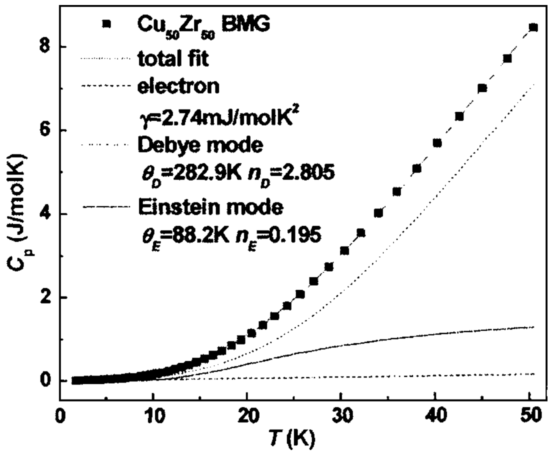

FIG. 4. The fitting results (the solid line) of the specific heat of the $Cu_{50}Zr_{50}$ BMG between 1.8 K and 50.5 K. The dotted and dashed-dotted lines represent contributions from the Debye mode and Einstein mode, respectively; the dashed line is the contribution of electrons.

ogy with that of spin-$\frac{1}{2}$ particles in a magnetic field,[6] the total entropy of the tunneling states can be calculated by $\Delta S = n \cdot R \ln 2$;here n (the density of tunneling states per atom) is constant, and R is the gas constant and the value of n of the BMG is calculated to be 1.36×10^{-3}. For example, there are 1.36×10^{-3} mol atoms (or groups of atoms) in per mole atoms of the BMG in tunneling states.

In metallic glasses, the effect of the tunneling states is more obvious at several Kelvin which is greatly different from that in the insulating glasses. The density of tunneling states of the superconductive CuZr glasses below 1 K is about 10^{-6} order per atom similar to many insulating glasses, which is lower than that of the $Cu_{50}Zr_{50}$ BMGs at several Kelvin. While in the nonsuperconductive metallic glass, there are many conduction electrons, and the high density of tunneling states may be due to conduction electrons assisted tunneling, which is required by the electron' dephasing quantum theory.[14,17]

The specific heat of solids in wide temperature range normally can be explained by Debye model

$$C_D = n_D \cdot 3R\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{\xi^4 e^{\xi}}{(e^{\xi}-1)^2} d\xi,$$

where θ_D is Debye temperature, n_D is a constant (usually $n_D=3$ in solids) and stands for the Debye oscillator strength per mole. When the electrons' contribution, γT [γ is determined in Fig. 1(b)] is subtracted, the specific heat from 1.8 to 50.5 K of the BMG cannot be fitted by the Debye model. So the Debye model, applied in the simplest way, cannot quantitatively explain the experimental results, and an additional quantized Einstein oscillator is required to model the specific heat of the BMG in the wide temperature range. As illustrated in Fig. 4, a model calculation including the contributions of one Debye mode and one Einstein mode leads to an adequate description of the experimental data. The solid line through the specific heat data in Fig. 4 represents a fit to the equation

$$C_p = \gamma T + C_D + n_E \cdot C_E. \quad (2)$$

$\gamma T(\gamma=2.74\ \text{mJ/mol K}^2)$ is shown in Fig. 4 by the dashed line; C_D, shown in the dotted line, represents contribution of the Debye mode with $\theta_D=282.9$ K and $n_D=2.805$; C_E, and the dashed-dotted line in Fig. 4, is the contribution of the Einstein mode

$$C_E = R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2},$$

with an Einstein temperature $\theta_E=88.2$ K and $n_E=0.195$ that stands for the Einstein oscillator strength per mole. The fact that one Einstein mode is required to model the data indicates the presence of the localized harmonic vibration mode in the BMG.[13] In metallic compounds with the oversized cage structure or large voids or enough large free volume, some atoms or metallic ions are weakly bound and occupy the oversized cages or voids, and the vibrations of these loose "rattler" atoms are regarded as resulting in the independent localized harmonic modes;[18–23] The localized mode is directly correlated to the density and size of voids. Recently, a model for the structure of metallic glasses consisting of the closely packed clusters (which is efficiently packed solute-centered atomic cluster) is proposed,[24] and these interstitial intercluster sites are filled with additional solute component atoms. The model is useful for understanding short and medium range order in BMGs and allows predictions of new glassforming alloy composition.[24] Meanwhile, the model helps to understand the low temperature properties. In metallic glasses' structure, the vibrations of some solute atoms could act as loose or weakly bound atoms in the interstitial intercluster sites, and the vibration of these loose "rattler" atoms are regarded to induce the independent localized modes. The case is similar to the localized harmonic vibrational modes found in some compounds and nanomaterials.[18–23]

The low-energy vibrational spectra of many glasses deviate in a characteristic way from Debye's plane-wave density of states, the excess modes being designated as the "boson peak."[19,25,26] There are many opinions as to the origin of the boson peak. Presently two hypotheses prevail: the localized vibrational modes and the collective propagating modes.[25] We have measured the specific heat at low temperatures for a variety of typical BMGs currently available, and find that the existence of the Einstein oscillators seems to be ubiquitous in BMGs. In typical ZrTiCuNiBe BMG, the boson peak determined by both neutron scattering[27] and specific heat[13] is ascribed to the localized vibrations. It is assumed that the localized vibrational mode (Einstein mode) has a Gaussian distribution with a main frequency corresponding to the Einstein frequency. Then the mode's contribution to the vibrational density of states has a Gaussian distribution,[13,20] and we can determine the vibrational spectrum with a peak by the specific heat of CuZr BMG.[13]. The Einstein oscillator in CuZr BMG induces the deviation of the vibrational density of state from the Debye squared-frequency law, and the excess state may be correlated with the boson peak. Following the neutron scattering results of the glassy $Cu_{46}Zr_{54}$ alloy,[28] the frequency ω distribution is roughly proportional to $\omega^{4/3}$

between 4.7 meV and 7 meV, and deviates the Debye spectrum ω^2. Our specific heat result below 50 K is in agreement with that of the neutron scattering,[28] and the localized mode is helpful in understanding the nature of the boson peak in the BMGs.

In conclusion, the binary CuZr BMG shows obvious tunneling states effect at several Kelvin by the low-temperature specific heat and electronic resistivity. The density of tunneling states in the BMG is much higher than the typical value in insulating glasses below 1 K. The entropy of the tunneling states cannot be explained simply by Schottky-type specific heat anomaly. The localized mode, which is correlated with the boson peak, is found in the simple metallic glass.

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