Supplemental Materials

Size effects of low-temperature excess heat capacity in the $Cu_{50}Zr_{50}$ film metallic glasses

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1. Figure S1

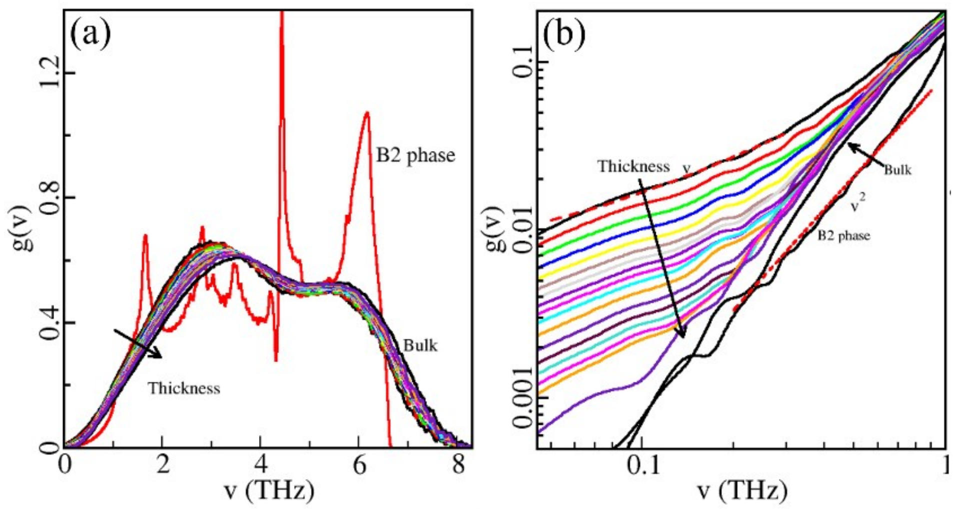

Figure S1 (a) The vibrational density of states (VDOS) in $Cu_{50}Zr_{50}$ bulk, film metallic glasses and B2 crystalline phase; (b) VDOS (v<1 THz) in double logarithmic coordinates of the $Cu_{50}Zr_{50}$ bulk, film metallic glasses and B2 crystalline phase. The fitted curves are shown in dashed lines;

2. Figure S2

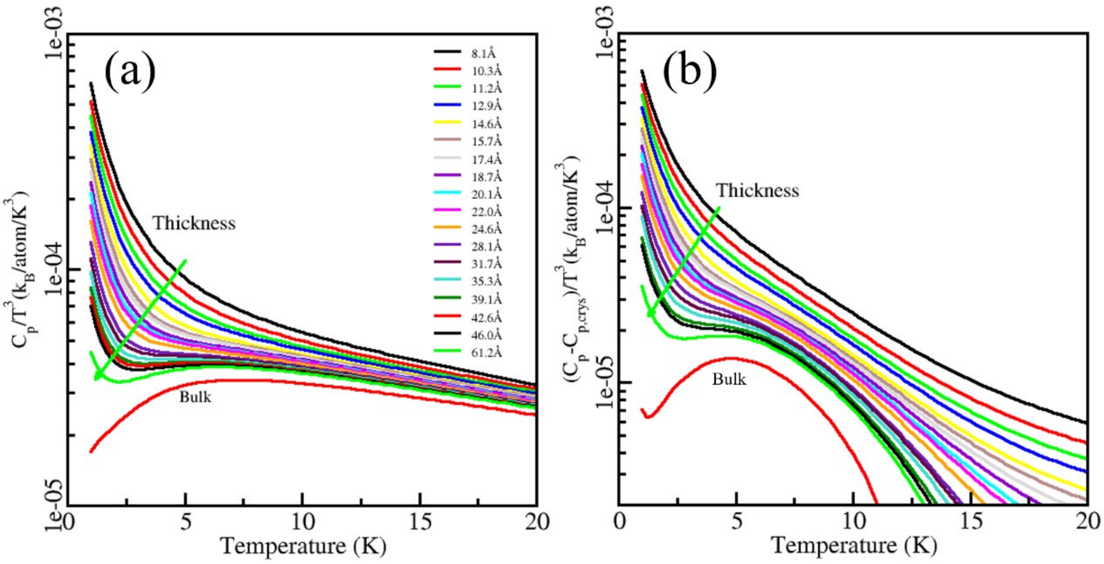

Figure S2 The heat capacity (a) C_p / T^3 and (b) $(C_p - C_{p,crys}) / T^3$ of the bulk and film metallic glasses with the thickness ranging from 8.1 Å to 61.2 Å, respectively. The lowest red line in (a) and (b) represents the heat capacity of the bulk metallic glass. The heat capacity of $Cu_{50}Zr_{50}$ B2 crystalline phase is regarded as the reference in (b).

3、The reason for choosing the formula in fitting the excess heat capacity

In the film with the thickness $d \geq 15.7$ Å, bulk-like atoms emerge in the films. So, the mole specific heat can be calculated by the formula:

$$C_{p,m} = \lim_{\Delta T\to 0}\frac{\Delta Q}{n\Delta T} = \lim_{\Delta T\to 0}\frac{\Delta Q^s + \Delta Q^b}{n\Delta T}$$
$$= \lim_{\Delta T\to 0}\frac{n^s C^s_{p,m}\Delta T + n^b C^b_{p,m}\Delta T}{(n^s + n^b)\Delta T}$$
$$= C^b_{p,m} + \frac{n^s (C^s_{p,m} - C^b_{p,m})}{(n^s + n^b)}$$
$$= C^b_{p,m} + \frac{d^s A\rho^s (C^s_{p,m} - C^b_{p,m})}{dA\overline{\rho}}$$
$$= C^b_{p,m} + \frac{d^s (C^s_{p,m} - C^b_{p,m})\rho^s / \overline{\rho}}{d}$$

The absorbed heat of the film metallic glasses can be roughly divided into two parts: absorbed by the surface atoms $\Delta Q^s = n^s C^s_{p,m}\Delta T$ and by the bulk-like atoms $\Delta Q^b = n^b C^b_{p,m}\Delta T$. In the above formula, $C^s_{p,m}$ and $C^b_{p,m}$ are the mole specific heat of the surface atoms and the bulk-like atoms, respectively. $n^s = d^s A\rho^s$ and n^b are the amount of the surface atoms and bulk-like atoms in the substance, respectively. d^s is the thickness and A is the area of the film. Furthermore, the total amount of the substance is $n = n^s + n^b = dA\overline{\rho}$, where ρ^s and $\overline{\rho}$ are the number density of the surface atom and the average number density of the film, respectively. Based on the above consideration, the excess heat capacity of the film can be written as:

$$\left(C_p(d) - C_{p,crys}\right)/T^3\Big|_{T=5K} = \left(C^b_{p,m} \text{-} C^{crys}_p\right)/T^3 + \frac{d^s (C^s_{p,m} - C^b_{p,m})\rho^s / T^3\overline{\rho}}{d} = a + b/d\,,$$

where a and b are parameters. By using the formula, the excess heat capacity can be well fitted.