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1990 J. Phys.: Condens. Matter 2 809

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## A further study on the new internal friction peak of the metallic glass $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ near $T_g$

Li Xiao-Guang<sup>†</sup>, Zhang Yuheng<sup>†</sup> and He Yizhen<sup>‡</sup>

<sup>†</sup> Department of Physics, University of Science and Technology of China, 230026 Hefei, People's Republic of China

<sup>‡</sup> Institute of Solid State Physics, Academia Sinica, 230031 Hefei, People's Republic of China

Received 22 May 1989

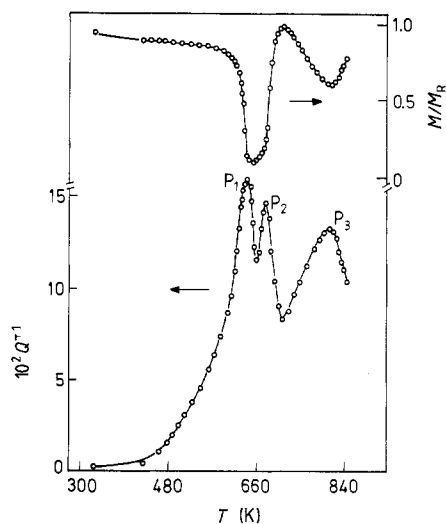
**Abstract.** In this work we studied in detail the internal friction of the metallic glass  $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$ , which can be regarded as a model material due to the relatively large difference between its glass transition temperature  $T_g$  and crystallisation temperature  $T_c$ . Three internal friction peaks,  $P_1$ ,  $P_2$  and  $P_3$  were observed using an inverted torsion pendulum in the temperature range 300–870 K. Using the cluster model and the free volume theory we discuss qualitatively and semi-quantitatively the behaviour of internal friction, relaxation time, activation energy and activated volume near  $T_g$ .

### 1. Introduction

Internal friction, especially, of thermal activated atomic relaxation origin has been studied intensively since the appearance of a new class of the metallic glasses. The internal friction related to thermal activated atomic relaxation can be divided into two categories: one is caused by small atoms such as hydrogen, called Snoek-like ordering [1], and another is due to structural changes of the glassy state itself such as structural relaxation [2, 3], glass transition [4, 5] and crystallisation [6, 7]. Our knowledge of the thermodynamic and/or kinetic processes of transformation from a metastable disordered state to stable crystalline states has been extended to studying the behaviour of internal friction during crystallisation.

Recent studies on the new internal friction peak associated with the glass transition provides experimental evidence that aids the understanding of the phenomenon of glassy solid–liquid transition, which is an important topic in the physics of amorphous solids. Moron and co-workers [8] pointed out that if the temperature of crystallisation is higher than that of glass transition, then a new effect may appear that exhibits some of the characteristics of migrational relaxation. It is worth noting that some workers have attempted to use the concept of synergism to investigate the characteristics of structural changes near  $T_g$  [9], and this seems to be a useful approach, as it is supported by experimental results [4].

A large number of experimental results has shown that internal friction of metallic glasses can be affected by various factors as a result of the changes of the glassy structure



**Figure 1.** The temperature dependence of internal friction  $Q^{-1}$  and shear modulus  $M$  of the metallic glass  $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$  with a heating rate of  $5 \text{ K min}^{-1}$  (as-received specimen).

[2–11]. But so far, the relationship between the behaviour of internal friction and these microprocesses is not clearly understood.

A detailed study has been performed of the internal friction behaviour of the metallic glass  $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$  during glass transition or in the region of the glass transition temperature to elucidate the physics of glass transition.

## 2. Experimental

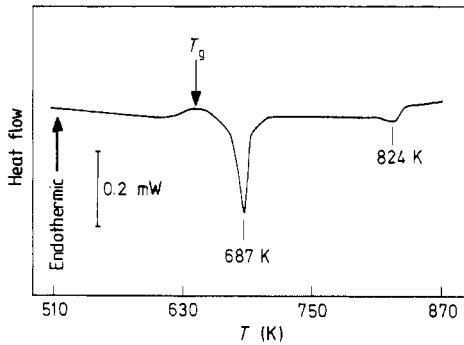
Internal friction was measured in the temperature range 300–870 K using a simple inverted torsion pendulum. Samples of the Pd–Cu–Si metallic glass was provided by the Institute of Precious Metals, China National Non-Ferrous Metal Industry Corporation. It was produced by using melt-spinning technique (for which a rapidly spinning copper wheel was used). The composition of the ribbon was Pd:77.5 at.%, Cu:6 at.%, Si:16.5 at.%. The dimensions of the specimens cut out from the ribbon for these experiments were about  $0.05 \times 1.5 \times 25 \text{ mm}^3$ . The heating rate varied from  $2 \text{ K min}^{-1}$  to  $10 \text{ K min}^{-1}$  and the cooling rate was about  $6 \text{ K min}^{-1}$  in the temperature range investigated.

When measuring the effect of tensile stress on internal friction, stress was applied to the specimens by increasing the counterbalance weight.

## 3. Results and analysis

### 3.1. General behaviour of internal friction and shear modulus of $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$

The temperature dependence of internal friction and shear modulus of metallic glass  $\text{Pd}_{77.5}\text{Cu}_6\text{Si}_{16.5}$  (as-received) in the temperature range 300–870 K is shown in figure 1. Three internal friction peaks,  $P_1$ ,  $P_2$  and  $P_3$  are observed at  $T_{P_1} = 640 \text{ K}$ ,  $T_{P_2} = 678 \text{ K}$  and  $T_{P_3} = 807 \text{ K}$ , respectively, with a heating rate of  $5 \text{ K min}^{-1}$ . The height of the  $P_1$



**Figure 2.** Differential scanning calorimetry (DSC) endotherm during isochronal heating (scan rate  $5 \text{ K min}^{-1}$ ).

peak is higher than that of  $P_2$  or  $P_3$ . The shear modulus decreases rapidly with increasing temperature near  $T_{P_1}$  and then increases in the temperature region of  $P_2$ . A second minimum observed on the modulus curve corresponds to the internal friction peak  $P_3$ . The variation of the first two peaks with temperature differs from that reported earlier on the other glassy alloys [6].

Differential scanning calorimetry (DSC) measurements show two exothermic peaks in the temperature region of the internal friction peaks  $P_2$  and  $P_3$ , and the internal friction peak  $P_1$  is found to be near the glass transition region ( $T_g \approx 635 \text{ K}$ ) on the DSC curve, as shown in figure 2.

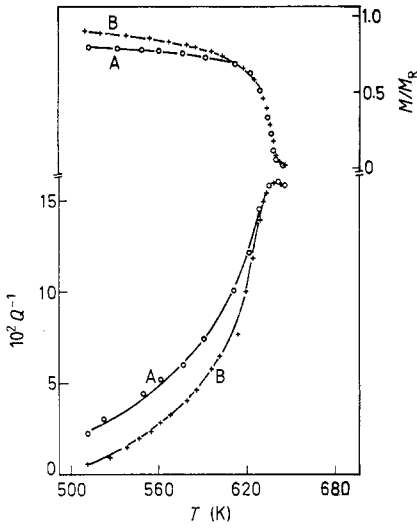
### 3.2. The repeatability and reversibility of $P_1$

During isochronal experiments, the appearance of peak  $P_1$  can be repeated on the same specimens from run to run. The position and the height of  $P_1$  do not change obviously even though the temperature exceeds  $T_{P_1}$  by about 10 K during the measurements, and neither does the shear modulus, as shown in figure 3. The repeatability and/or reversibility of  $P_1$  implies that the structural changes should also be reversible during heating and cooling between quasi-equilibrium states. For decreasing temperature the position of the  $P_1$  peak shows a slight shift to a lower temperature, see figure 4. Internal friction peaks  $P_2$  and  $P_3$  are not reversible, as shown in figures 5 and 6.

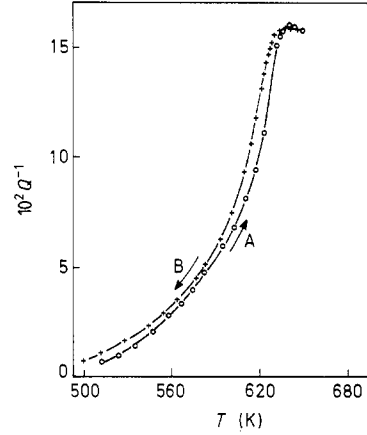
### 3.3. The main relaxation characteristics—relaxation time $\tau$ and activation energy $E$ of $P_1$

The appearance of the  $P_1$  peak can be related to a stress-induced aftereffect. Since although  $T_{P_1}$  shifts to higher temperatures with increasing frequency, the height of  $P_1$  changes very little (as shown in figure 7), the behaviour of  $P_1$  should be of the relaxation type. The positions of  $P_2$  and  $P_3$  do not vary with frequency but their heights decrease as frequency increases. It is evident that the origin of these peaks ( $P_2$  and  $P_3$ ) is different from that of  $P_1$ .

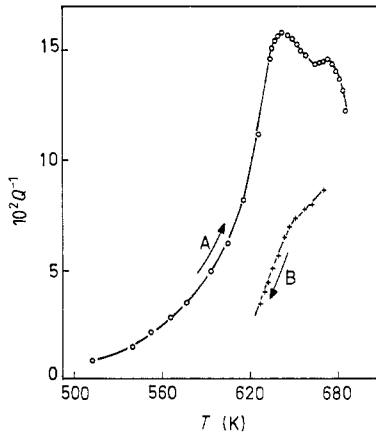
From the frequency dependence of  $T_{P_1}$ , one can therefore estimate the relaxation time  $\tau$  and activation energy  $E$  corresponding to  $P_1$  in the glass transition region.



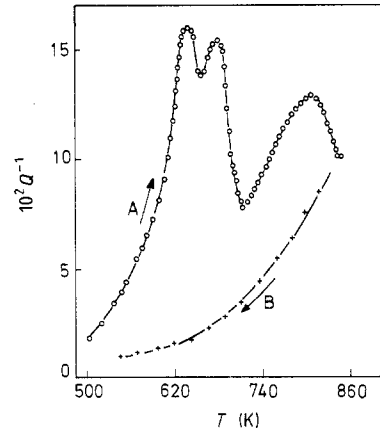
**Figure 3.** Behaviour of internal friction and shear modulus in the temperature range 500–670 K (scan rate 5 K min<sup>-1</sup>). Curves A, first run; curves B, second run on the same specimen.



**Figure 4.** The temperature dependence of internal friction during scanning with temperature increasing and temperature decreasing on the same specimen. Curve A, second run with heating rate 5 K min<sup>-1</sup>; curve B, just after curve A, with cooling rate 6 K min<sup>-1</sup>.



**Figure 5.** Internal friction  $Q^{-1}$  versus temperature  $T$ , showing the irreversibility of the  $P_2$  peak. Curve B was obtained just after curve A.

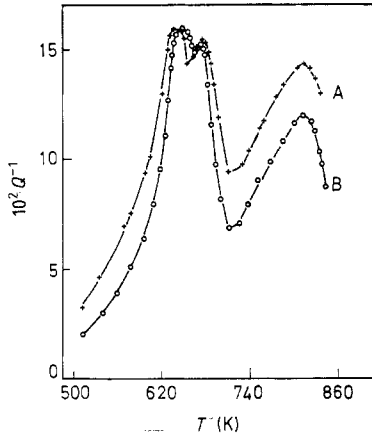


**Figure 6.** Plot of  $Q^{-1}$  versus  $T$ , showing the irreversibility of the  $P_3$  peak.

However, should we assume that the relaxation time  $\tau$  near  $T_g$  can be described by an Arrhenius expression

$$\tau = \tau'_0 \exp(E/kT) \tag{1}$$

where  $\tau'_0$  is pre-exponential factor,  $E$  is activation energy and  $k$  is the Boltzmann



**Figure 7.** Plot of  $Q^{-1}$  versus  $T$ , showing the effect of frequency: curve A,  $f_R = 0.2043$  Hz ( $f_R$  being the frequency at room temperature); curve B,  $f_R = 0.6703$  Hz.

constant. If  $\tau'_0$  and  $E$  are regarded as constants, one will find that  $\tau'_0 \sim 10^{-40}$  s, and this is much too small for real materials. In fact, the jump of atoms or atomic clusters under the action of a stress should be directly associated with the distribution of the free volume.

We propose the use of the free volume model for estimation of the relaxation time  $\tau$  and activation energy  $E$  related to the internal friction peak  $P_1$  in the following. The most probable distribution of free volume is [12]

$$p(v) \sim \exp(-\gamma v/V_f) \tag{2}$$

where  $\gamma$  is a geometrical factor approximately equal to unity, and  $V_f$ , the total free volume can be expressed as

$$V_f = A(T - T_0) \tag{3}$$

where  $A$  is proportional to the thermal expansion coefficient in the vicinity of  $T_g$ , and  $T_0$  is the temperature at which  $V_f$  goes to zero ( $T_0$  being equal to 505 K for the metallic glass  $Pd_{77.5}Cu_6Si_{16.5}$  [13]). Assume  $V^*$  to be the minimum free volume where an atomic cluster can be accommodated. The atomic clusters will move in the direction of the stress and the probability per second,  $\Gamma$  ( $= \tau^{-1}$ ), of such a jump is proportional to the probability of having a free volume exceeding  $V^*$ , namely

$$\Gamma = \text{constant} \int_{V^*}^{\infty} p(v) dv = \Gamma_0 \exp(-\gamma V^*/V_f). \tag{4}$$

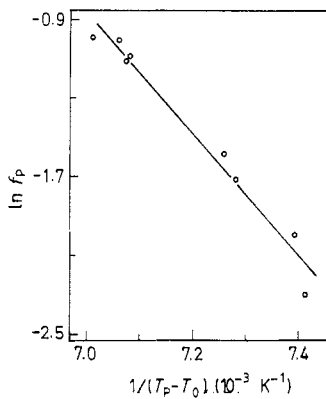
Therefore, the time for completing such a jump, i.e. the relaxation time, can be expressed as

$$\tau = \Gamma^{-1} = \tau_0 \exp[B_1/(T - T_0)] \tag{5}$$

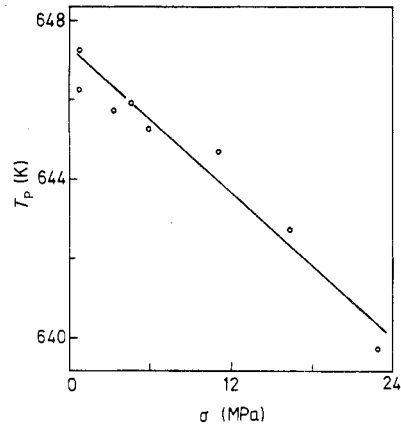
where  $\tau_0 = \Gamma_0^{-1}$  and  $B_1 = \gamma V^*/A$ . This is similar to the Vogel-Fulcher equation. Since

$$2\pi f_p \tau = 1 \tag{6}$$

where  $f_p$  is the frequency at the  $P_1$  peak, one can obtain a linear relationship between  $\ln f_p$  and  $1/(T - T_0)$  as shown in figure 8 with  $B_1 \approx 3056$  K and  $\tau_0 \approx 2 \times 10^{-10}$  s.



**Figure 8.** Plot showing the linear relationship between  $\ln f_p$  and  $1/(T_p - T_0)$ .



**Figure 9.** Plot showing stress dependence of the temperature ( $T_{P_1}$ ) at which the  $P_1$  peak occurs.

The value of  $\tau_0$  obtained is larger than that for the jump of a single atom, and this implies that in this temperature region the entities concerned are probably atomic clusters and/or atoms. When the values of  $B_1$  and  $\tau_0$  are known, one can obtain the activation energy  $E$  near the glass transition temperature  $T_g$ .

Following the assumption that  $E$  changes with temperature,

$$E = k d \ln \tau / d(1/T) \quad (7)$$

and combining equations (5) and (7), we have

$$E = kB_1 [T/(T - T_0)]^2. \quad (8)$$

Thus,

$$E_{P_1} |_{640-646K} \approx 5.9-5.5 \text{ eV}.$$

Since the value of the activation energy decreases with increasing temperature, we believe that the atomic clusters move cooperatively in the vicinity of  $T_g$ , and this is more difficult than the diffusion of single atoms in the glassy matrix, so the activation energy is larger than it would be for single atoms.

Although  $T_{P_1}$  varies with frequency, the shift of  $T_{P_1}$  may not be very large because of the relatively large activation energy corresponding to  $P_1$ . Of course, if the frequency is high enough,  $T_{P_1}$  will shift to the temperature region of crystallisation, and thus the behaviour of  $P_1$  must be affected by the process of crystallisation. On the other hand, if the frequency is low enough,  $T_{P_1}$  would shift to a lower temperature. But, in this case, since the measuring time is very long in relative terms, crystallisation would also occur at such a high temperature. However, how one is to separate quantitatively the variation of physical properties caused by the superposition of both glass transition and crystallisation is still a problem.

#### 3.4. The mean size of the atomic clusters associated with $P_1$

Various factors which affect the size, shape and rate of transportation of atomic clusters will influence the physical properties of metallic glasses near  $T_g$  or  $T_x$ . Figure

9 shows that the temperature of the P<sub>1</sub> peak decreases with increasing tensile stress  $\sigma$  applied to the as-received specimens during internal friction measurements, and the tensile stress ( $\sigma$ ) dependence of  $T_{P_1}$  is given by

$$T_{P_1} = B_2 - B_3\sigma \quad (9)$$

where  $B_2 = 646.5$  K and  $B_3 = 2.9 \times 10^{-7}$  K Pa<sup>-1</sup>. From equation (9), we can estimate the value of the activated volume during transportation of atomic clusters.

Combining equations (5), (6), (8) and (9), we have

$$B_1 = 3056 - [B_3 \ln(1/\omega\tau_0)]\sigma$$

and

$$E = E_0 - \Delta V^*\sigma$$

where  $\omega = 2\pi f$ ,  $E_0 = 3056k[T/(T - T_0)]^2$  and  $\Delta V^* = kB_3[T/(T - T_0)]^2 \ln(1/\omega\tau_0)$ .  $\Delta V^*$  may be regarded as the activated volume. If  $\ln(1/\omega\tau_0) \sim 20$ , then

$$\Delta V^* \sim 1.6 \text{ nm}^3. \quad (10)$$

From this, one can estimate the mean size ( $S$ ) of the atomic clusters moved under the action of the applied stress, as

$$S \sim 1.5 \text{ nm}.$$

This value is approximately equal to that of a minimum short-range ordering domain [14]. The above analysis shows that  $\Delta V^*$  decreases with increasing temperature and this agrees with the variation of cluster size in the model earlier proposed by us [4].

The estimated values of activation energy  $E$ , relaxation time  $\tau$  and activated volume  $\Delta V^*$  are only semi-quantitative but they seem to be quite useful in the understanding of the behaviour of the internal friction peak P<sub>1</sub> (which should be controlled by the cooperative motion of atomic clusters rather than diffusion of some single atoms in glassy matrix).

As a model material, the larger temperature difference between glass transition and crystallisation ( $\Delta T = |T_g - T_x|$ ) of the glassy alloy Pd<sub>77.5</sub>Cu<sub>6</sub>Si<sub>16.5</sub> makes it possible to study the physics of glassy solid-liquid transition at an atomic level by the internal friction technique without the intervention of the glass-crystalline solid transformation.

## Acknowledgments

This work was partly supported by the Post-doctoral Foundation of China. The authors wish to thank Zheng Fuqian of the Institute of Precious Metals (People's Republic of China) for supplying the specimens.

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