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LOW TEMPERATURE LONG-TIME RELAXATION IN GLASSES

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1. Introduction

Experimental investigations of various amorphous solids show that the long-time heat relaxation is probably one of those low-temperature characteristics (together with the heat capacity, the heat conductivity and other anomalies) that distinguish amorphous solids from crystalline ones. Glassy-type power release $\dot{Q}(T_1, T_0, t)$ after rapid cooling from the temperature T_1 to the temperature T_0 is approximately proportional to t^{-1} in a wide range of t (10^{-6}sec $\leq t \leq 10^{+6}$sec).

Up to now, this heat release was observed in vitreous silica /1-4/, amorphous metals /6,7/, and some disordered organic materials /4,5,8/. In crystalline solids this long-time relaxation may be due to the tunnelling of dilute hydrogen atoms (Nb-Ti-H /4/) or due to some "glassy" properties of the electric-dipole system in ferroelectrics with diffuse phase transition /9,10/.

The standard tunnelling theory /11,12/ with a constant distribution function $P(\Delta, \lambda)=P=$const of two-level systems (tls) (Δ is the asymmetry energy of double-well potential, λ is the tunnelling parameter), time dependent density of states

$$n(E,t) = n_0(t) = (P/2)\ln(4t/\tau_{min}) \quad , \qquad (1)$$

and power released (or absorbed for $T_1 < T_0$)

$$\dot{Q}(T_1, T_0, t) = (\pi^2 k_B^2/24)\bar{P}V(T_1^2 - T_0^2)t^{-1} \qquad (2)$$

(τ_{min} is the shortest relaxation time, E is the energy of tls, V is the volume of the specimen) explains experimental results for T_1, $T_0 < 2$K well, and $\bar{P}$ can be determined. (Deviations from pure t^{-1} dependence are essential in ferroelectric

$Pb_{0.915}La_{0.085}(Zr_{0.65}Ti_{0.35})O_3$ (PLZT) only, where $\dot{Q} \sim t^{-1}\exp\cdot(-t/\tau_{max})$ with T_1-dependent τ_{max} /9/.

Essential deviations from the standard tunnelling theory are observed for temperatures T_o, $T_1 > 2K$, which will be discussed in this paper. The materials investigated in this temperature range are shown in the table.

Table

Material	t-Dependence	Measuring Time	T_o, K	$\bar{P}_m$, 10^{37} /Jg	T_f, K	Reference
vitreous silica	t^{-1}	10h ÷ 200h	0.05	4.5	13	ref. 4
$Fe_{80}B_{14}Si_6$	t^{-1}	0.5h ÷ 60h	1.3	2.3	20	ref. 7
$Co_{69}Fe_{4.5}Cr_2Si_{2.5}B_{22}$	t^{-1}	0.5h ÷ 40h	1.3	1.2	24	ref. 7
epoxy resin	$t^{-0.76}$	0.2h ÷ 700h	1.1÷1.9	100	16.5	ref. 8
PLZT (polycrystalline)	$t^{-1}\exp(-t/\tau_{max})$	0.1h ÷ 5h	1.3	14.3	7.5	ref. 9

2. T_1 dependence

The analysis of experiments with $T_1 > 2K$ and $T_o \leq 1.3K$ leads to a modification of the tunnelling theory: the maximum energy $E_f = k_B/T_f$ of the energy distribution of the density of states is included,

$$n(E,t) = n_o(t)/(1 + \exp(E-E_f)/k_BT_b)), \qquad (3)$$

where $n_o(t)$ is determined by eq. (1). With distribution (3), the heat release is

$$\dot{Q}(T_1,T_o,t) = (\pi^2k_B^2/24)\bar{P}V(I_2(T_1/T_f,T_b)T_1^2 - I_2(T_o/T_f,T_b)T_o^2)t^{-1} \quad , \qquad (4)$$

where

$$I_2(T/T_f,T_b)=2(T_f/T)^2\int_0^{T/T_f}(T/T_f)I_1(T/T_f,T_b)d(T/T_f) \quad , \qquad (5)$$

$$I_1(T/T_f,T_b) = (6/\pi^2)\cdot\int_0^{\infty}\frac{x^2\exp(-x)dx}{(1+\exp(-x))^2(1+\exp(xT/T_f-1)/(T_b/T_f)))} \quad . \qquad (6)$$

If $T_o/T_f \leq 0.1$, $I_2(T_o/T_f,T_b) \simeq 1$, and

$$\frac{24\dot{q}t}{\pi^2k_B^2\bar{P}_mT_1^2} + T_o^2/T_1^2 = I_2(T_1/T_f,T_b) \quad , \qquad (7)$$

$\dot{q} = \dot{Q}(T_1,T_o,t)/m$, $\bar{P}_m = \bar{P}V/m$ and m is the specimen mass.

The universal curve (7) corresponds to the experiment well (see fig. 1 and the table). The parameters $\bar{P}_m$ are deter-

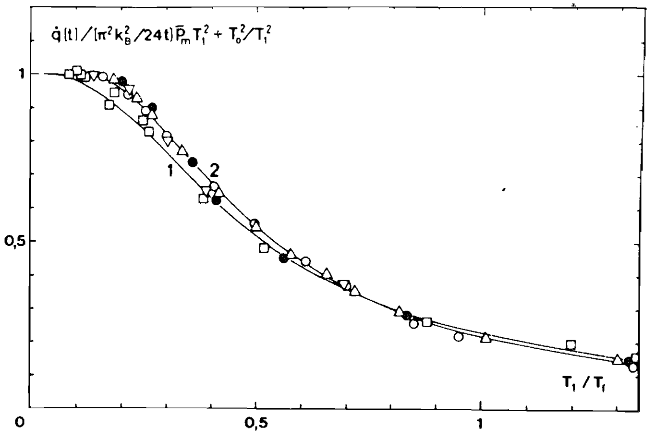

Fig. 1. The T_1-dependence of power release $\dot{Q}(T_1,T_o,t)$ for $T_o/T_f \leq 0.1$, presented according to eq. (7). ▽ - vitreous silica /4/, ○ - $Fe_{80}B_{14}Si_6$ /6,7/, △ - $Co_{69}Fe_{4.5}Cr_2Si_{2.5}B_{22}$ /6,7/, □ - epoxy resin /8/, ● - PLZT /9/. (P_m, T_f and T_o see in the table). Curve 1 and 2: integral I_2, calculated from eq. (5) and (6) for $T_b/T_f = 0.2$ and $T_b = 0$ respectively.

mined from eq. (2), valid for $T_1 < 0.2T_f$. Their values are of the same order as those calculated from the heat capacity, heat conductivity or ultrasonic measurements. Unexpected low values of E_f ($7.5\mathrm{K} \le T_f \le 24\mathrm{K}$) indicate that the low-temperature anomalies are due to critical or soft potentials in amorphous solids. The theory of soft modes, developed recently /13-16/, predicts the existence of a universal energy $w/k_B = (10 \div 30)\mathrm{K}$ in glasses and good agreement with the standard tunnelling theory for $E \ll w$ only. If $E > w$, the thermal activation process dominates. Then the density of states of tls for large tunnelling parameters (large relaxation time) decreases essentially. The calculated value of w agrees with the experimental E_f very well. Therefore, the T_1 dependence of the power release is probably similar to that in fig. 1 for all glasses. Real distribution functions may differ from (3), as I_2 is rather insensitive to the exact form of the energy dependence of $n(E)$, but decreasing $n(E)$ to zero in the vicinity of E_f is necessary to explain the experimental results.

The experimental value E_f of the polycrystalline ferroelectric PLZT is in surprisingly good agreement with E_f of amorphous solids. The glasslike behaviour of PLZT is probably due to soft potential as well.

3. T_o dependence

According to the assumption of the soft mode potential barriers of the order w, deviations from eqs. (2) and (4), experimentally observed in epoxy resin at $T_o > 2\mathrm{K}$ /8/, are expected. Though such deviations were not studied in experiments with other glasses, "short-heating measurements" indicate that dependence of $\dot{Q}$ on T_o/T_f is probably also a universal one. Such measurements are performed as follows. After complete relaxation at T_o the specimen is heated rapidly to the "heating" temperature T_H and after the interval t_H rapidly cooled to T_o again; then the heat release $\dot{Q}(T_H, T_o, t_H, t)$ is measured. If the tunnelling parameter did not depend on the temperature, the ratio of $\dot{Q}$'s for two different t_H (and the same T_o and T_H) would be independent of T_H /7/:

$$r = \frac{\dot{Q}(T_H, T_o, t_{H1}, t)}{\dot{Q}(T_H, T_o, t_{H2}, t)} = \frac{1 + t/t_{H2}}{1 + t/t_{H1}}. \qquad (8)$$

All experimental r from measurements with two amorphous metals /6,7/ and epoxy resin /8/ (with $t_{H1} = 0.5\mathrm{h}$ and $0.2\mathrm{h}$, $t_{H2} = 20\mathrm{h}$, $t = 1\mathrm{h}$) are the same for the same T_H/T_f and t/t_{H1}, being independent of the material (see fig. 2). In contrast to eq. (8), the ratio r increases with T_H/T_f for $T_H/T_f > 0.1$. Assuming $\acute{\lambda} = \lambda - \alpha T/T_f$, where λ is temperature independent and α is constant, we get /7/:

$$r = \frac{1 + (t/t_{H2})\exp(-\alpha T_{H2}/T_f)/\exp(-\alpha T_o/T_f)}{1 + (t/t_{H1})\exp(-\alpha T_{H1}/T_f)/\exp(-\alpha T_o/T_f)} \qquad (9)$$

in good agreement with experimental results not only with amorphous solids, but also with PLZT ($t_H/t = 0.5$, $t_H = 5$ min). However, more data on a wider variety of glasses are necessary to determine the correct form of the T_o (and T_H) dependence of $\dot{Q}$.

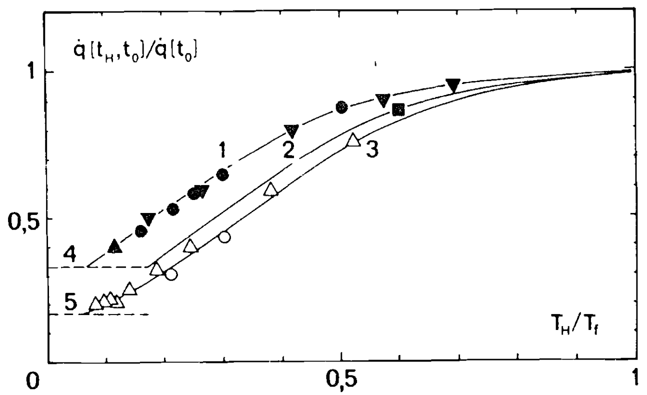

Fig. 2. The ratio of the power released after short heating time t_H $\dot{q}(t_H, t_o)$ and long heating time $\dot{q}(t_o)$, (t_H = 20h) at $t=t_o$ depending on T_H/T_f for various materials. ● - $Fe_{80}B_{14}Si_6$, t_H = 0.5h, t_o = 1h; T_f = 20K; ○ - $Fe_{80}B_{14}Si_6$, t_H = 0.2h, t_o = 1h, T_f = 20K; ▼ - $Co_{69}Fe_{4.5}Cr_2Si_{2.5}B_{22}$, t_H = 0.5h, t_o = 1h, T_f = 24K; △ - epoxy resin, t_H = 0.5h, t_o = 1 h, T_f = 16.5K; ■ -PLZT, t_H = 5 min, t_o= 10 min, T_f = 7.5K;

Curve 1: eq. (9) with $\alpha = 6$, $t_H/t_o = 0.5$, T_o = 1.3K, T_f = 20K. Curve 2: eq. (9) with $t_H/t_o = 0.2$, $\alpha = 6$, T_o = 1.3K, T_f = 7.5K. Curve 3: eq. (9) with t_H/t_o = 0.2, $\alpha = 6$, T_o = 1.3K, T_f = 20K. Curve 4: eq.(8) with t_H/t_o = 0.5. Curve 5: eq. (8) with t_H/t_o = 0.2.

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Салинг С., Салинг А.Л., Колач М. E8-87-577

Низкотемпературная медленная термическая релаксация в стеклах

Проведен анализ экспериментальных результатов по низкотемпературному медленному тепловыделению на материалах, исследованных при температурах выше 1К. Значительные отклонения от туннельной теории в этой области температур можно объяснить, исходя из предположения о существовании максимальной энергии E_f, которая ограничивает распределение по энергии туннельных состояний и высоту потенциальных барьеров. E_f слабо зависит от материала /$7,5К \le E_f \le 24К$/. Результаты согласуются с теорией мягких потенциалов.

Работа выполнена в Лаборатории ядерных проблем ОИЯИ.

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Low Temperature Long-Time Relaxation in Glasses

The analysis of low-temperature long-time heat release experiments for materials at temperatures above 1K is presented. The essential deviations from the tunnelling theory in this temperature range can be explained by the assumption of maximum energy E_f which limits the energy distribution of tunnelling states and the height of potential barriers. E_f is only slightly material dependent ($7.5K \le E_f \le 24K$).The results are consistent with the theory of soft potentials.

The investigation has been performed at the Laboratory of Nuclear Problems, JINR.

Preprint of the Joint Institute for Nuclear Research. Dubna 1987