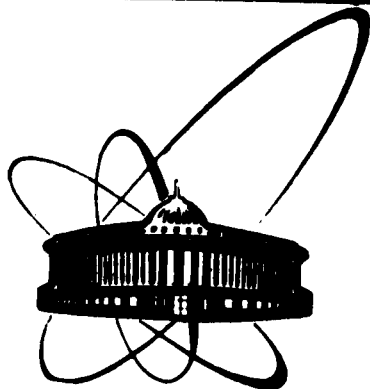


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ОБЪЕДИНЕННЫЙ  
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LOW TEMPERATURE LONG-TIME ENERGY  
RELAXATION IN  $\text{LiCl} \cdot 7\text{H}_2\text{O}$

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## INTRODUCTION

The most low-temperature anomalies of amorphous solids can be explained by the phenomenological tunnelling theory<sup>/1,2/</sup> assuming that two-level systems (TLS) (due to the tunnelling of atoms) with a broad distribution of their energies and relaxation times exist. Only three model parameters, namely: the distribution parameter  $\bar{P}$ , describing a distribution independent of the energy  $E$  and the tunnelling parameter  $\lambda$

$$P(E, \lambda) = \bar{P} = \text{constant}, \quad (1)$$

and the coupling parameters  $\gamma_1$  and  $\gamma_t$ , describing the coupling between the TLS and phonons, are necessary for calculation of various physical parameters.

A fundamental question is the correlation between the low-temperature anomalies and the glass transition temperature  $T_g$ . From the thermal conductivity data of various amorphous solids, it was deduced that  $\bar{P}$  is proportional to  $T_g^{-1}$  in accordance with the free volume model<sup>/3/</sup>, assuming the coupling parameters to be constant<sup>/4/</sup>. The same result was obtained by heat capacity measurements on water-doped nitrat glasses<sup>/5/</sup> and ultrasonic measurements on fluoride and silicate glasses<sup>/6-10/</sup>. Recently acoustic experiments have been performed with electrolyte glasses ( $\text{LiCl} \cdot n\text{H}_2\text{O}$ ,  $\text{ZnCl} \cdot n\text{H}_2\text{O}$ ) exhibiting very low glass transition temperatures. The obtained values of  $\bar{P}_\gamma^2$  can be explained by the assumption that  $\gamma$  is proportional to  $T_g$  and

$$\bar{P} = P_0 \exp(\epsilon/kT_g), \quad (2)$$

where  $P_0 = 5.3 \cdot 10^{44} \text{ j}^{-1} \text{ m}^{-3}$  and  $\epsilon/k = 630\text{K}^{/11/}$ . Moreover, the  $\bar{P}$ -values calculated with eq.(2) for larger  $T_g$  are in quite good agreement with the results of the above-mentioned experiments. However, investigations of the dielectric susceptibility of  $\text{LiCl} \cdot n\text{H}_2\text{O}$  yield significantly smaller  $\bar{P}$ -values than expected from eq.(2)<sup>/12/</sup>.

For an independent examination of eq.(2), the heat capacity and the power released after the rapid cooling of the sample were measured for  $\text{LiCl} \cdot 7\text{H}_2\text{O}$ .

According to the tunnelling theory the distribution parameter can be determined from the linear term of the heat capacity  $a(t) = c(t)/T$

$$\bar{P} = 12 a(t) / k^2 \pi^2 \ln(4t / \tau_{\min}), \quad (3)$$

or from the power  $\dot{Q}(T_1, T_0, t)$  released or absorbed after a rapid temperature change from the equilibrium temperature  $T_1$  to  $T_0$

$$\bar{P} = 24 V t \dot{Q}(T_1, T_0, t) / k^2 \pi^2 (T_1^2 - T_0^2), \quad (4)$$

where  $\tau_{\min}$  is the shortest relaxation time and  $V$  is the volume of the specimen.

Thus both measurements allow a direct determination of  $\bar{P}$  and the corresponding density of states (DOS) of TLS:

$$n(E, t) = n_0(t) = (\bar{P}/2) \ln(4t / \tau_{\min}). \quad (5)$$

However, the calculation of  $\bar{P}$  from the heat capacity data is connected with some serious drawbacks.

1. As a rule,  $\tau_{\min}$  is unknown and must be calculated from /14/

$$\tau_{\min} = 2 \pi \rho \hbar^4 / (\gamma_\ell^2 v_\ell^{-5} + \gamma_t^2 v_t^{-5}) E^3 \coth(E/2kT), \quad (6)$$

with  $E \approx 2kT$ , where  $\rho$  is the mass density and  $v$  is the sound velocity.

2. The low temperature heat capacity anomaly can be caused not only by TLS, but also by defects, impurities or electrons (in the case of metals).

3. The energy dependence of the density of states (DOS) cannot be obtained for higher energies, because above a few kelvins the phonon contribution to the heat capacity dominates.

The heat release measurement - free of these drawbacks - is therefore more convenient for the DOS determination and its energy dependence. However, it is necessary to take into account that only TLS with relaxation times larger than the time required for cooling or heating the sample contribute to the power released or absorbed, i.e. only information about the distribution  $P(E, \lambda)$  with large  $\lambda$  will be obtained.

## EXPERIMENTAL

A special calorimeter with a low heat leak ( $\dot{Q}_B = 0.5 \text{ nW}$ ) to the sample was used in our experiments. An aluminium container (with or without the electrolyte glass) hung in a vacuum chamber on 8 kapron threads. The container was connected with a Ge-thermometer, a heater and a copper wire to provide the thermal contact with a mechanical heat switch.

For the heat release study the resistance drift  $\dot{R}$  of the thermometer was measured as a function of time  $t$  after the rapid cooling of the specimen from the equilibrium temperature  $T_1$  (where the specimen remained for at least 24hr) to  $T_0 = 4.2 \text{ K}$  or  $T_0 = 1.5 \text{ K}$ . The corresponding power release  $\dot{Q}(T_1, T_0, t)$  was then determined from the measured power release  $\dot{Q}_m$ , the power  $\dot{Q}_A$  due to the thermal contact between the specimen and the body of the calorimeter, and the heat leak  $\dot{Q}_B$ :

$$\dot{Q}(T_1, T_0, t) = \dot{Q}_m - \dot{Q}_A - \dot{Q}_B, \quad (7)$$

where

$$\dot{Q}_m = \dot{R}C / (\delta R / \delta T), \quad (8)$$

$$\dot{Q}_A = A(T_K - T). \quad (9)$$

$C$  is the heat capacity of the container with or without the electrolyte glass,  $\delta R / \delta T$  is the sensitivity of the thermometer, and  $A$  is the total thermal resistance of the kapron threads and the electrical wires to the heater and the thermometer. The sample temperature was chosen close to the calorimeter temperature  $T_K$ , which was kept constant (to  $10^{-4} \text{ K}$ ). When  $T(t) - T_K = 10^{-2} \text{ K}$ , the sample temperature was set to  $T_0 = T_K$ .

First, the heat capacity and the power release of the hollow container (174.7g aluminium, 17.4g copper) was measured. As expected, no long-time heat release was observed. After the cooling of the container from  $T_1 = 10 \text{ K}$  to  $T_0 = 1.5 \text{ K}$  in 8 min the heat leak  $\dot{Q}_B = 0.5 \text{ nW}$  was measured and the constant  $A = 0.1 \text{ nW/mK}$  was determined. The accuracy of the power release measurement is given by the fluctuations of  $\dot{Q}_B$ , which are smaller than  $0.1 \text{ nW}$  (tested during one week).

The  $\text{LiCl} \cdot 7\text{H}_2\text{O}$  solution was prepared from pure  $\text{LiCl}$  and deionized water. To control the  $\text{LiCl}$  concentration, the refraction coefficient  $n_r(20^\circ\text{C}) = 1.394$  was measured, yielding  $n = 6.5$  and  $T_g = 139 \text{ K}$  according to ref.14.

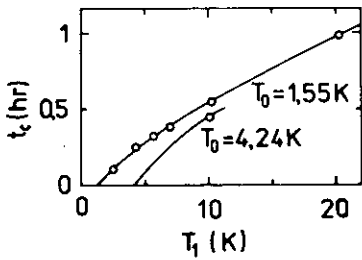


Fig. 1. Time  $t_c$  necessary for cooling the sample from  $T_1$  to  $T_0 = 1.5$  K or  $T_0 = 4.2$  K.

The container with the electrolyte glass was cooled down from room temperature to 78 K with a cooling rate of about 3 K/min. After the cooling of the sample from 78 K to 4.2 K in 3 hr, the power release was measured at 4.2 K for 200 hr. However, even after 200 hr the power release was significantly larger (of about 5 nW) than the neat leak  $\dot{Q}_B$  and a correction of the measured power release after cooling the sample from 4.2 K to 1.5 K and 2.52 K to 1.5 K was necessary. As a rule, the sample was kept at various  $T_1$  for 24 hr and measured at 1.5 K for 12 hr. For  $T_1 \approx 10$  K the power release was also measured after cooling to 4.2 K. The time  $t_c$  required for the cooling of the container with the electrolyte glass from  $T_1$  to  $T_0 = 1.5$  K and  $T_0 = 4.2$  K is shown in fig. 1.

## RESULTS AND DISCUSSION

In the temperature range  $1.5 \text{ K} \leq T \leq 10 \text{ K}$  equation

$$c/T = a + bT^2 \quad (10)$$

with  $a = 11.3 \mu\text{J/gK}^2$  and  $b = 13.9 \mu\text{J/gK}^4$  yields a good fit of the heat capacity data of  $\text{LiCl} \cdot 7\text{H}_2\text{O}$ . From the linear term of the heat capacity the distribution parameter  $\bar{P} = (31 \pm 6) \cdot 10^{44}/\text{Jm}^3$  can be obtained, where the values  $t = 200 \text{ s}$ ,  $\tau_{\text{min}} = 1.4 \text{ ns}$ ,  $\rho = 1.166 \text{ g/cm}^3$  ( $\rho$  is the mass density) and eq. (3) were used.  $\tau_{\text{min}}$  was calculated from eq. (5) with  $v_\ell = 4 \cdot 10^3 \text{ m/s}$ ,  $v_t = 2 \cdot 10^3 \text{ m/s}$ ,  $\gamma_\ell = 0.47 \text{ eV}$ ,  $\gamma_t = 0.33 \text{ eV}^{1/2}$  and  $\rho = 1.166 \text{ g/cm}^3$ . Since the heat capacity measurements were performed only above 1.5 K, and a massive aluminium container was used, the  $\bar{P}$ -value is connected with a large error.

In fig. 2 the power release  $\dot{Q}(T_1, T_0, t)$  after the rapid cooling of the sample from various equilibrium temperatures  $T_1$  to  $T_0 = 1.5$  K or 4.2 K is shown. For all  $T_1$ ,  $T_0$  and  $3t_c < t < 12 \text{ hr}$  an accurate  $t^{-1}$  dependence of the power release was found.

Note, that very large values of the heat release were observed. After cooling the sample from  $T_1 = 20.3 \text{ K}$  to  $T_0 = 1.5 \text{ K}$ , the limit of the accuracy of our apparatus (0.1 nW) will be

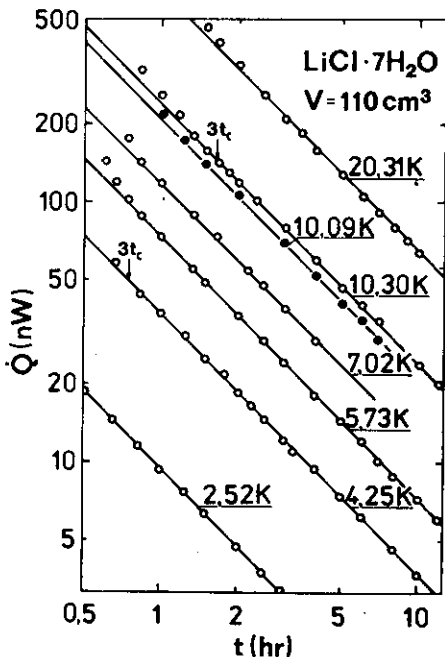


Fig.2. The power  $\dot{Q}$  released in  $\text{LiCl}\cdot 7\text{H}_2\text{O}$  after the rapid cooling of the sample from different  $T_1$  to 1.5 K (o) or 4.2 K (o). Straight lines:  $\dot{Q}$  proportional to  $t^{-1}$ .

obtained only after 6000 hr, assuming that the time dependence of the power release will not change. Nevertheless, the power release is significantly smaller than expected. For  $T_1 < 10$  K, the temperature dependence of the power release agrees with eq.(4) and we obtain  $\bar{P} = (10.1 \pm 0.3) \cdot 10^{44} / \text{Jm}^3$ , which is significantly smaller than the value  $\bar{P} = 5.1 \cdot 10^{46} / \text{Jm}^3$  calculated from eq.(2) with  $T_0 = 139$  K, however it agrees quite well with  $\bar{P} = (31 \pm 6) \cdot 10^{44} / \text{Jm}^3$

and  $\bar{P} = (21 \pm 5) \cdot 10^{44} / \text{Jm}^3$  calculated from our heat capacity data and the dielectric susceptibility data of ref.12 respectively. The discrepancy is probably due to the coupling parameters. The dielectric measurements yield  $\gamma_1 = 0.47$  eV and  $\gamma_t = 0.33$  eV<sup>12/</sup>, while in ref.11 the larger  $\bar{P}$  values were obtained with  $\gamma_1 = 0.1$  eV and  $\gamma_t = 0.07$  eV assuming that  $\gamma$  is proportional to  $T_g$ .

Figure 3 shows the distribution parameter calculated with eq.(4) from the long-time power release data of vitreous silica<sup>13/</sup>,  $\text{Fe}_{80}\text{B}_{14}\text{Si}_6$ <sup>14/</sup>, epoxy resin<sup>15/</sup> and  $\text{LiCl}\cdot 7\text{H}_2\text{O}$  as a function of  $T_r$ . It is seen that  $\bar{P}$  increases with decreasing  $T_g$ . In particular, the  $\bar{P}$ -value of  $\text{LiCl}\cdot 7\text{H}_2\text{O}$  ( $T_g = 139$  K) is about 10 times larger than in vitreous silica ( $T_g = 1470$  K) in accordance with the assumption that  $\bar{P}$  is proportional to  $T_g^{-1}$ . However, more long-time power release data of various amorphous solids are necessary to determine the relation between  $T_g$  and  $\bar{P}$  exactly.

For  $T_1 > 10$  K the  $\bar{P}$ -values calculated with eq.(4) from the power release data of  $\text{LiCl}\cdot 7\text{H}_2\text{O}$  decrease with increasing  $T_1$ . Similar deviations from the assumption  $P(E, \lambda) = \bar{P} = \text{constant}$  were found for all investigated amorphous solids (s.fig.3).

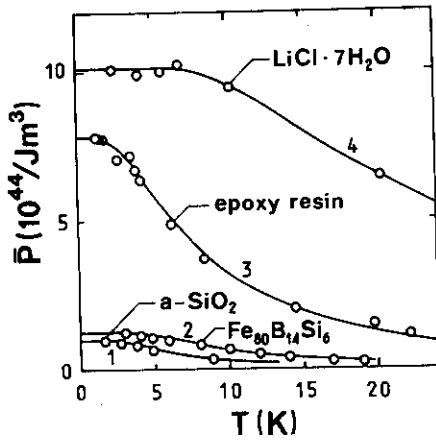


Fig.3. The distribution parameter  $\bar{P}$  calculated with eq.(4) from the power release data of vitreous silica<sup>/13/</sup>,  $\text{Fe}_{80}\text{B}_{14}\text{Si}_6$ <sup>/14/</sup>, epoxy resin<sup>/15/</sup> and  $\text{LiCl}\cdot 7\text{H}_2\text{O}$  as a function of  $T_1$ . Curves: function (12) calculated with the energy dependent DOS(eq.11). The following fit parameters were used: 1 -  $\bar{P}=1.0\cdot 10^{44}/\text{Jm}^3$ ,  $E_f/k = 13$  K,  $T_b = 0$  K, 2 -  $\bar{P} = 1.3\cdot 10^{44}/\text{Jm}^3$ ,  $E_f/k = 20$  K,  $T_b = 0$  K, 3 -  $\bar{P} = 7.8\cdot 10^{44}/\text{Jm}^3$ ,  $E_f/k = 16.5$  K,  $T_b = 3.3$  K, 4 -  $\bar{P} = 10.1\cdot 10^{44}/\text{Jm}^3$ ,  $E_f/k = 48$  K,  $T_b = 0$  K.

There are at least two possibilities to explain this behaviour in the framework of the tunnelling theory: first, the DOS could not extend beyond energies above a cut-off energy  $E_f$ , or second, an upper limit  $\lambda_{\max}$  of the distribution function could exist. Indeed, the first assumption yields a good fit for all investigated amorphous solids<sup>/16/</sup> (including  $\text{LiCl}\cdot 7\text{H}_2\text{O}$ ) and structural glasses<sup>/17,18/</sup>, using for calculation of  $\dot{Q}$  the energy dependent DOS

$$n(E, t) = n_0(t) / (1 + \exp((E - E_f) / kT_b)) , \quad (11)$$

where the fit parameters  $E_f$  and  $T_b$  are constant and  $n_0$  is given by eq.(5). In this case the function

$$f(T_1, T_0) = 24 Vt \dot{Q}(T_1, T_0, t) / (T_1^2 - T_0^2) \quad (12)$$

decreases with increasing  $T_1$  if  $T_1 > 0.2 E_f/k$ , and  $f(T_1, T_0) = \bar{P} = \text{constant}$  if  $T_0, T_1 < 0.2 E_f/k$  (s.fig.3).

However, the  $T_0$  dependences of  $\dot{Q}$ , which was yet obtained at higher temperatures only for epoxy resin<sup>/15/</sup>, cannot be explained either by the first or by the second assumption<sup>/18/</sup>. The deviations of the time and temperature dependence of the power release at higher temperatures is probably due to a temperature dependent relaxation process, as, for example, the thermal activation. A detailed analysis of this problem will be given in a future paper.

#### 4. CONCLUSIONS

Measuring the heat capacity and the power release, the distribution parameter  $\bar{P} = (31 \pm 6) \cdot 10^{44}/\text{Jm}^3$  and  $\bar{P} = (10.1 \pm 0.3) \cdot 10^{44}/\text{Jm}^3$  of TLS in  $\text{LiCl} \cdot 7\text{H}_2\text{O}$  were obtained. These  $\bar{P}$ -values agree well with  $\bar{P} = (21 \pm 5) \cdot 10^{44}/\text{Jm}^3$  calculated from the dielectric susceptibility data<sup>/12/</sup>, and they are significantly smaller than expected from the acoustic experiments<sup>/11/</sup> and eq.(2). In accordance with the assumption that  $\bar{P}$  is proportional to  $T_g^{-1}$ , the DOS of TLS in  $\text{LiCl} \cdot 7\text{H}_2\text{O}$  is about 10 times larger than in vitreous silica.

In contrast to other investigated glasses the temperature dependence of the power release in  $\text{LiCl} \cdot 7\text{H}_2\text{O}$  agrees with the tunnelling theory up to very large  $T_1$  ( $T_1 < 10$  K).

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#### REFERENCES

1. Anderson W., Halperin B.I., Varma C.N. - Phil.Mag., 1972, 25, p.1.
2. Phillips W.A. - J.Low Temp.Phys., 1972, 7, p.352.
3. Cohen M.H., Grest G.S. - Solid State Commun., 1981, 39, p.143.
4. Reynolds C.L. - J.Non Cryst.Solids, 1979, 30, p.371.
5. Raychchaudhuri A.K., Pohl R.O. - Solid State Commun., 1981, 37, p.105; Phys.Rev., 1982, B31, p.1090.
6. Doussineau P., Matecki M., Schön W. - J.Phys.Collog. (Paris), 1982, 43, C9-493; J.Phys.(Paris), 1983, 44, p.101.
7. Piche L. et al. - Phys.Rev.Lett., 1974, 32, p.1426.
8. Hunklinger S., Piche L. - Solid State Commun., 1975, 17, p. 1189.
9. Jäckle J. et al. - J.Non Cryst.Solids, 1976, 20, p.365.
10. Golding G., Graebner J.E., Kane A.B. - Phys.Rev.Lett., 1976, 37, p.1248.
11. Reichert U., Schmidt M., Hunklinger S. - Solid State Commun., 1986, 57, p.315.
12. Röhring V. - Dissertation, Heidelberg 1988.
13. Schwark M. et al. - J.Low Temp.Phys., 1985, 59, p.55.



14. Sahling S. et al. - J.Low Temp.Phys., 1986, 65, p.289.
15. Kolač M. et al. - J.Low Temp.Phys., 1987, 68, p.285.
16. Sahling S., Sahling A., Kolač M. - Solid State Commun., 1988, 65, p.1031.
17. Sahling S., Sahling A., Kolač M. - J.Low Temp.Phys., 1988, 73, p.450.
18. Sahling A., Sahling S. - JINR, E8-89-315, Dubna, 1989, to be published in J.Low Temp.Phys.

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