

# How Universal are the Low Temperature Acoustic Properties of Glasses?

**J.F. Berret**

Laboratoire de Science des Matériaux Vitreux, Université de Montpellier, France

**M. Meißner**

Hahn-Meitner Institut, Berlin, Germany

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We evaluated already published data on ultrasound absorption and velocity changes below 1 K for a set of 18 different glasses. By uniformly analysing these data according to the tunnelling model we have calculated the standard spectral density  $\bar{P}$  of two-level-systems (TLS) and their coupling energy  $\gamma_l$  and  $\gamma_t$  to longitudinal and transversal phonons. Contrary to literature, we have not observed any correlation between  $\bar{P}$  and the glass transition temperature  $T_g$  for our set of 18 glasses. As far as  $T_g$  is concerned we only found a relation  $\tau_{\min}^{0.1K} \propto T_g^n$  with  $n \simeq 2.5$  and where  $\tau_{\min}$  is the shortest TLS-phonon relaxation time at 0.1 K. Since the values for  $\bar{P}$  and  $\gamma_{l,t}$  scatter within half an order of magnitude, we conclude that the TLS parameters of a certain glass are only weakly dependent on bulk properties. We find that the ratio  $\gamma_t^2/C_{44}$  (where  $C_{44}$  is the shear elastic constant) is a more sensitive parameter for tests on the variation of the TLS spectral density of glasses.

## I. Introduction

At low temperatures, i.e. below  $\sim 1$  K, structurally and orientationally disordered solids exhibit so called “universal thermal and acoustic properties” [1]. This “glassy behaviour” of a variety of disordered materials, such as dielectric glasses, metallic glasses, amorphous polymers and even crystals with different kinds of disorder [2], has successfully been ascribed to the existence of two-level tunnelling systems (TLS), intrinsic to the disordered state [3]. However, among this broad variety of disordered solids a unified physical picture of the TLS entities has not been accomplished, yet. So far, the low energy excitations observed in thermal and acoustic measurements have been characterized by parameters provided by the tunnelling model: the number density of TLS states  $\bar{P}$  (assuming a constant distribution of potential double well asymmetries and tunnelling parameters) and the

coupling energy  $\gamma_{l,t}$  of the TLS (which is due to interaction with elastic waves). Initially, it was assumed that if the TLS were actually intrinsic elements to the disordered state, a survey on a variety of glasses would reveal correlations between the microscopic TLS parameters and fundamental macroscopic quantities characterizing the glassy state. In the past experimental data were reviewed systematically for numerous amorphous systems, predominantly with respect to thermal conductivity [4–7], specific heat [4, 5], and ultrasonic attenuation and dispersion [8]. Some of the above mentioned studies gave evidence for a dependence  $\bar{P} \propto 1/T_g$ , where  $T_g$  is the glass transition temperature [4, 5, 8]. This experimental result is supported by a theory [9] on the free volume  $V_F$  of a glass, where  $V_F$  originates from a number of configurational states. If  $N$  states are distributed over the energy range  $k_B T_g$ , the TLS density of states would result in  $\bar{P} \propto V_F/T_g$ . Very recently, Reichert et al. [10, 11] reported a

stronger dependence  $\bar{P} \propto \exp\{E_0/k_B \cdot T_g\}$ , which is based on a survey of different glasses ranging between  $T_g \simeq 140 \dots 1400$  K.

Similar to recent studies on the universal thermal conductivity of glasses [6, 7], we shall also follow the idea of a certain universality of TLS in disordered solids and will present a critical re-examination of ultrasonic data already published for 18 glassy materials of different chemical compositions and bonding characters. We have analysed ultrasonic attenuation and dispersion experiments below 1K with respect to the standard tunnelling model and shall present a unified analysis of all the 18 glasses. After evaluating the TLS parameters (as described in Sect. II) we shall then search for correlations between the low temperature based parameters and quantities commonly used to characterize the frozen-in glassy state. In Sect. III we shall discuss some of the results with respect to a variation on  $T_g$  and the elastic constant  $C_{44}$ , respectively. On the 18 glasses studied, we do not observe a correlation between  $\bar{P}$  and  $T_g$ ; instead we observe the spectral density ranging around a value  $\bar{P} \simeq (1.5 \pm 1) \cdot 10^{45} \text{J}^{-1} \cdot \text{m}^{-3}$ . Within this range we find some evidence on a dependence of  $\bar{P}$  on the ratio  $\gamma_t^2/C_{44}$  which relates the origin of TLS to interaction via elastic stress waves as it has been proposed by Klein et al. [12].

## II. Selection of a Set of Glasses

At low temperatures  $T < 1$  K acoustic properties of disordered solids exhibit a typically anomalous behaviour. By means of ultrasonic techniques the dispersion and absorption observed for longitudinal and transverse acoustic waves (mainly for frequencies between 10 MHz and 10 GHz) can well be described in terms of the phenomenological tunnelling model [13]. This model assumes a broad distribution of two-level-systems (TLS) as far as their energy splittings and relaxation times are concerned. The TLS and the propagating elastic waves interact via resonant and relaxational mechanisms. According to the standard tunnelling picture, the resonant interaction of a TLS and an acoustic mode of frequency  $\gamma = \omega/2\pi$  results in a relative velocity change [13]

$$\left(\frac{\Delta v}{v}\right)_{1,t} = C_{1,t} \cdot \ln(T/T_0) \quad (1)$$

and in an unsaturated absorption [13]

$$\alpha_{1,t} = \frac{\pi \cdot C_{1,t} \cdot \omega}{v_{1,t}} \tanh\left(\frac{\hbar \cdot \omega}{2 \cdot k_B \cdot T}\right) \quad (2)$$

where  $T_0$  is an arbitrary reference temperature and

$$C_{1,t} = \frac{\bar{P} \cdot \gamma_{1,t}^2}{\rho \cdot v_{1,t}^2}, \quad (3)$$

here  $\rho$  is the mass density and  $\bar{P}$  is the spectral density (number of TLS per unit volume and energy),  $v_{1,t}$  are the longitudinal and transverse sound velocities and  $\gamma_{1,t}$  are the coupling constants of TLS, due to the TLS-phonon interaction.

The relaxational contribution to absorption is due to 1-phonon-processes and shows an asymptotic behaviour to [13]

$$\alpha_{1,t} = \frac{\pi^4 \cdot C_{1,t} \cdot K_3}{96 \cdot v_{1,t}} T^3 \quad (4)$$

where

$$K_3 = \frac{4 \cdot k_B^3}{\pi \cdot \rho \cdot \hbar^4} \left( \frac{\gamma_l^2}{v_l^5} + \frac{2\gamma_t^2}{v_t^5} \right). \quad (5)$$

Compared to the resonant part (1), the contribution of the velocity change due to relaxation is negligible. In summary, below 1 K resonant interaction mechanisms dominate the dispersion of an acoustic wave, whereas absorption is produced by the relaxational processes.

Treating  $C_l$ ,  $C_t$  and  $K_3$  as independent fitting parameters the experimental acoustic data can consistently be fitted according to (1) and (4). In this way we determine the characteristic TLS-quantities, spectral density  $\bar{P}$  and coupling constants  $\gamma_{1,t}$ . It should be pointed out that from (1) the slopes  $C_{1,t}$  can be determined to good confidence as dispersion data are available down to  $\sim 0.1$  K in most of the cases. Contrary to this, the parameter  $K_3$  is more difficult to determine because generally absorption measurements lack accuracy below  $\sim 0.5$  K. Unfortunately, it is just below this temperature, that a  $\alpha \propto T^3$ -dependence becomes evident. Taking into account data below 1 K only, the main problem remains, whether the evaluation of  $K_3$ -values for a set of different glasses is reliable.

In order to acquire a reliable set of data, glasses were selected from a variety of materials including oxides, polymers, semi-conductors, normal and superconducting metals, electrolyte solutions, ionic conductors, magnetic and orientational glasses by the following criterion: They had to show the typical low temperature glassy behaviour for the variation of sound velocity *and* attenuation for longitudinal *and/or* transverse polarization and be in good agreement with the tunnelling model.

From our initial set of available acoustic data in disordered solids [14], metallic and superconducting glasses were eliminated, since here it is not only phonons, but also electrons that play an important role

in the relaxational processes [13, 15]. Therefore, (1) and (4) are not applicable any longer: The presence of two different kinds of relaxational mechanisms (due to electrons and TLS) contributing to absorption and a comparably strong  $T$ -dependence results in a difficult and dubious determination of TLS-parameters.

Finally, we settled on 18 non-metallic glasses which fulfilled the above conditions. Best fits were performed using (1) and (4). The fitting parameters  $C_l$ ,  $C_t$ ,  $K_3$  as well as the density  $\rho$ , the velocities  $v_l$ ,  $v_t$  and the glass transition temperature  $T_g$  are listed in Table 1. The chemical composition of those glasses which are named by trade names are listed in Ref. [16]. Several of the 18 samples, the fluorozirconate glasses, BK7, amorphous silica [8] and the series of Se-Ge alloys [17], have already been analysed according to comparable criteria. We note, that 5 types of structural glasses are represented, for which  $T_g$  varies on one order of magnitude (between 140 K for LiCl-7H<sub>2</sub>O and 1475 K for SiO<sub>2</sub>).

In order to compensate for the absence of low temperature data for one of the two polarizations (see Table 1), we utilize empirical approximations relating the velocities and coupling constants of the longitudinal and transverse modes. Taking into account sound velocity data only, we find in Fig. 1 a linear relation between  $v_l$  and  $v_t$  (within the given range of velocity values). The straight line in Fig. 1 is due to a best fit, and the missing velocities  $v_l$  and  $v_t$  have been calculated accordingly. As for 8 of the glasses the slopes of the logarithmic  $T$ -dependence of the relative velocity

change were only available for one of the two polarizations, we checked the remaining 10 complete sets of data for an empirical relation between  $\gamma_l$  and  $\gamma_t$ . From the ratio  $C_l/C_t$  of these glasses, we derived an average ratio of the squared coupling energies  $(\gamma_l/\gamma_t)^2 = 2.5$ . Assuming that this ratio also holds for the 6 other glasses [18] we determined  $\gamma_l$  for As<sub>2</sub>S<sub>3</sub>, LaSF-7, LiCl-7H<sub>2</sub>O, PS, PC and epoxy resin, accordingly. Although the above relations are based on data for 12 different glasses only, we note that the results remain the same, even if the set of structural insulating glasses was extended [14].

The electrolyte LiCl-7H<sub>2</sub>O (salt content 12.6 mol.%) is of special interest because of its low glass transition temperature. Recently, for this and similar systems, such as ZnCl<sub>2</sub>-xH<sub>2</sub>O at various salt contents, TLS spectral densities have been reported to be 100 times higher than those in vitreous silica [10]. Clear experimental evidence is missing for a  $T^3$ -increase in the absorption for this material: In Ref. [19]  $T=0.45$  K is the lowest temperature that has been measured; however, we are able to fit the 104 MHz ultrasonic attenuation data reasonably well in the temperature range 0.5 . . . 17 K, using numerical integration derived from the tunnelling model [8]. In this fitting procedure we used the  $C_l$ -value found by  $\Delta v/v$ -measurements [20]. In spite of a rather large uncertainty of our determination of  $K_3 = (8 \pm 2) \cdot 10^9 \text{ K}^{-3} \text{ s}^{-1}$ , we can claim that the spectral density of LiCl-7H<sub>2</sub>O is of the order  $\bar{P} \simeq 1 \cdot 10^{45} \text{ J}^{-1} \text{ m}^{-3}$  which is much smaller than the

**Table 1.** Summary of the data available on the low temperature ( $T < 1$  K) acoustic properties for 18 selected glasses (for chemical compositions, see Ref. 16). The parameters used to fit the dispersion data,  $C_l$  and  $C_t$ , and absorption data,  $K_3$ , to the tunnelling model are defined in the text

Glass	$\rho$ kg/m <sup>3</sup>	$T_g$ K	Ref.	$v_l$	$v_t$ km/s	$C_l$	$C_t$ 10 <sup>-4</sup>	$K_3$ 10 <sup>9</sup> /K <sup>3</sup> .s	Ref.	$\gamma_l$	$\gamma_t$ eV	$\bar{P}$ 10 <sup>45</sup> /J.m <sup>3</sup>	Ref.
a-SiO <sub>2</sub>	2200	1473	[a]	5.80	3.80	3.1	2.9	0.4	[8]	1.04	0.65	0.8	[8]
BK7	2510	836	[10]	6.20	3.80	2.7	3.3	0.3	[8]	0.96	0.65	1.1	[8]
As <sub>2</sub> S <sub>3</sub>	3200	444	[c]	2.70	1.46	1.6	nd	1.9	[b]	0.26	0.17	2.0	—
LaSF-7	5790	957	[10]	5.64	3.60	1.2	nd	0.4	[d]	1.46	0.92	0.4	—
SF4	4780	693	[e]	3.78	2.24	2.2	2.8	1.3	[e]	0.72	0.48	1.1	—
SF59	6260	635	[e]	3.32	1.92	2.3	2.8	2.2	[e]	0.77	0.49	1.0	—
V52	4800	593	[8]	4.15	2.25	4.0	4.9	1.5	[8]	0.87	0.52	1.7	[8]
BALNA	4280	520	[8]	4.30	2.30	3.8	4.8	1.1	[8]	0.75	0.45	2.1	[8]
LAT	5250	723	[8]	4.78	2.80	3.8	3.7	0.7	[8]	1.13	0.65	1.4	[8]
a-Se	4300	304	[c]	2.00	1.05	1.2	2.2	5.2	[17]	0.25	0.14	2.0	[17]
Se <sub>75</sub> Ge <sub>25</sub>	4350	530	[f]	nd	1.24	nd	0.9	2.4	[17]	nd	0.15	1.0	[17]
Se <sub>60</sub> Ge <sub>40</sub>	4250	633	[f]	nd	1.44	nd	0.3	1.3	[17]	nd	0.16	0.4	[17]
LiCl-7H <sub>2</sub> O	1200	139	[10]	4.00	nd	7.2	nd	8.0	[10; 19]	0.62	0.39	1.4	—
Zn-Glass	4240	570	[g]	4.60	2.30	3.0	3.6	0.8	[g]	0.70	0.38	2.2	—
PMMA	1180	374	[h]	3.15	1.57	2.0	3.7	9.0	[h]	0.39	0.27	0.6	—
PS	1050	355	[h]	2.80	1.50	3.6	nd	3.0	[i]	0.20	0.13	2.8	—
PC	1200	418	[h]	2.97	nd	1.8	nd	5.00	[h]	0.28	0.18	0.9	—
Epoxy	1200	350	[j]	3.25	nd	2.8	nd	4.30	[j]	0.35	0.22	1.1	—

Index: l – longitudinal  
t – transverse

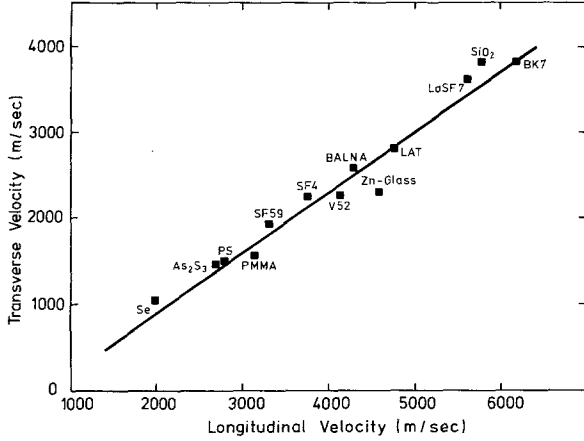


Fig. 1. Transverse versus longitudinal sound velocities for 13 glasses. The straight line is according to a least square fit (see text)

value of  $\bar{P} \simeq 50 \cdot 10^{45} \text{ J}^{-1} \text{ m}^{-3}$  reported in [10]; we shall discuss this discrepancy later on.

In Table 1 all numerical acoustic data which we used to calculate the 3 parameters  $\gamma_1$ ,  $\gamma_t$ , and  $\bar{P}$ , respectively, are presented. The references in block 2 refer to the original publications, where dispersion and absorption measurements down to  $T < 1 \text{ K}$  are reported. The references in block 3 refer to already published values for  $K_3$ ,  $\gamma_{1,t}$  and  $\bar{P}$  which we were able to confirm using (1) and (4). In cases where no references are given in block 3, the values have been obtained by our own analysis of dispersion and attenuation data.

We note that the TLS parameters can also be extracted from low temperature thermal measurements. From the very beginning of the study of glasses by Zeller and Pohl [21], specific heat and thermal conductivity measurements have been performed more extensively than acoustic measurements on disordered solids. Due to the distribution function  $P(E, \tau)$  of the tunnelling entities, the heat capacity of amorphous solids depends on temperature and on time. According to the standard tunnelling model assumption of a constant spectral density  $\bar{P}$ , the specific heat is [22]

$$C_p = \frac{\pi^2 \cdot k_B^2}{12 \cdot \rho} T \cdot \bar{P} \cdot \eta \quad (6)$$

where  $\eta = \ln(4 \cdot t / \tau_{\min})$  and  $\tau_{\min}$  is the shortest relaxation time of the TLS. As the majority of specific heat data published is unresolved in time (experimental time-scales range between  $\sim 0.1 \dots 100 \text{ s}$ ), only the product of  $\bar{P} \cdot \eta$  can be gained from experiments. Generally it is found that  $\eta \simeq 5 \dots 20$ . Thus, the density of states derived by this method is different from the spectral density derived from acoustic data. Apart from this, thermal conductivity measurements provide the prod-

uct of  $\bar{P} \cdot \bar{\gamma}^2$  only, where  $\bar{\gamma}$  defines a mode averaged coupling constant. In order to avoid these additional uncertainties we here present an analysis of TLS-parameters, strictly based on acoustic data.

### III. Discussion

As we outlined in the introduction, it is our purpose to search for evidence of correlations between TLS-parameters and macroscopic properties of glasses. In general, any physical characteristic of the glassy state could influence the TLS-parameters. Among numerous possibilities, the glass transition temperature  $T_g$  and the Debye temperature  $\theta_D$  have frequently been used to correlate high and low temperature properties of disordered solids.

The glass transition temperature roughly reflects the thermal energy scale where the structural disorder of the supercooled melt freezes. For many years a considerable interest has been taken in a relation  $\bar{P}$  vs.  $T_g$ . Cohen and Crest [9] presented a free volume model for an amorphous network from which a correlation  $\bar{P} \propto 1/T_g$  can be derived.

The Debye temperature characterizes the high frequency phonon limit of the phonon spectral distribution. However, due to the fact that the number of vibrating units in an irregular network is unknown, the value of  $\theta_D$  has limited utility, and the Debye velocity  $v_D = \left[ \frac{1}{3} \left( \frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{-\frac{1}{3}}$  is used to specify the stiffness of a glass. It is useful to write  $m \cdot v_D^2 / V$ , i.e. the elastic energy per unit volume as this quantity represents a combination of the elastic constants  $C_{11} = \rho \cdot v_l^2$  and  $C_{44} = \rho \cdot v_t^2$  of the glass. Klein et al. [12] have shown that in glasses strain interactions between different TLS-configurations can cause a broad distribution of energies  $P(E)$ , where the spectral density scales as  $\bar{P} \propto C_{ik} / \gamma^2$ . Below we shall present a check of this prediction.

We shall now start checking the variation of  $\bar{P}$  within our set of 18 glasses. As already mentioned above, we are not able to find evidence for any definite variation of  $\bar{P}$  vs.  $T_g$ . In Fig. 2 on a log-log scale the spectral density is displayed against the glass transition temperature. Despite the large scattering in the  $\bar{P}$ -data observed in Fig. 2, we notice that among the set of 18 glasses presented here the TLS spectral density remains in the range  $\bar{P} \simeq (0.5 \dots 2.5) \cdot 10^{45} \text{ J}^{-1} \text{ m}^{-3}$ . This result contradicts recent findings on much larger  $\bar{P}$ -values for electrolyte glasses with low  $T_g$  reported by Reichert et al. [10]. By Brillouin scattering techniques the low temperature dispersion  $\Delta v / v$  of electrolyte glasses,  $\text{LiCl} \cdot x\text{H}_2\text{O}$  ( $T_g = 138 \text{ K} \dots 148 \text{ K}$ ) and  $\text{ZnCl}_2 \cdot x\text{H}_2\text{O}$  ( $T_g = 164 \text{ K}, 188 \text{ K}$ ), has been measured, and the

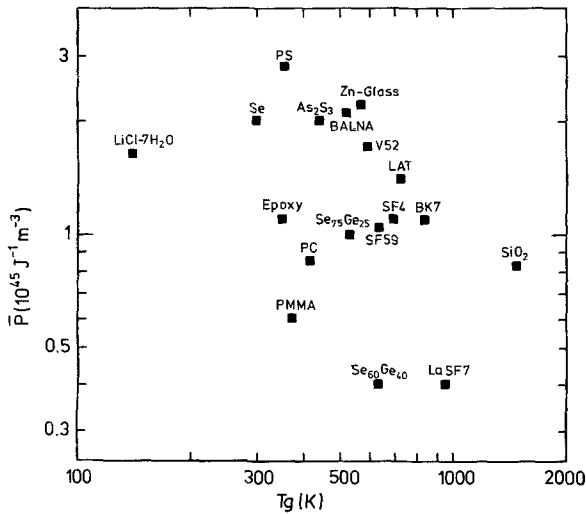


Fig. 2. Variation of the TLS spectral density  $\bar{P}$  with the glass transition temperature  $T_g$

corresponding  $\bar{P}$ -values have been calculated from the logarithmic slope of the velocity change using  $\gamma_1 \approx 0.10$  eV. This value was obtained by extrapolating a linear dependence  $\gamma_{1,t} \propto T_g$  to low  $T_g$  which had been checked on a set of different glasses. According to Ref. [10], the value  $\gamma_1 \approx 0.1$  eV for electrolyte glasses is supported by an experimental determination of the same value for amorphous water ( $T_g = 135$  K). Contrary to this, from the ultrasound measurements performed on LiCl-7H<sub>2</sub>O by Kaspers and Röhring [19], we find  $\gamma_1 = 0.62$  eV and  $\gamma_t = 0.39$  eV (see Table 1). Using the former values and taking into account the  $C_T$ -data determined by Reichert et al. [10] for both types of electrolyte glasses, the spectral densities of LiCl-xH<sub>2</sub>O and ZnCl<sub>2</sub>-xH<sub>2</sub>O would range around a value of  $\bar{P} = 1.5 \cdot 10^{45} \cdot \text{J}^{-1} \cdot \text{m}^{-3}$  which is in accordance with the variation we observed in Fig. 2. We suppose that more ultrasonic experiments on electrolyte glasses will be needed to solve this discrepancy of almost two orders of magnitude for  $\bar{P}$ . So far it seems that within our set of 18 glasses the spectral densities exhibit a more universal behaviour, i.e.  $\bar{P}$  varies around  $(1.5 \pm 1) \cdot 10^{-45} \text{J}^{-1} \cdot \text{m}^{-3}$  independent from the nature of chemical bonding and composition of a glass.

However, we also emphasize that in Fig. 2 a dependence  $\bar{P} \propto 1/T_g^n$  can be found for glasses belonging to the same class (as defined by the composition). This e.g. applies for the fluorozirconate glasses BALNA, V52 and LAT, where  $n \approx 1$  as originally found by Doussineau et al. [8]. For the amorphous semi-conductors As<sub>2</sub>S<sub>3</sub>, Se<sub>75</sub>Ge<sub>25</sub> and Se<sub>40</sub>Ge<sub>60</sub> one obtains  $n \approx 2$ . Furthermore,  $\bar{P} \propto 1/T_g$  has been found by Raychauduri and Pohl [4] on ionic Ca-K-nitrates, for which specific heat data have been taken into account, only.

With respect to the TLS-phonon coupling energy  $\gamma$  we are not able to confirm a linear dependence of the mean value  $\bar{\gamma}$  on the glass temperature  $T_g$  which is reported by Reichert et al. [10] and Doussineau et al. [8]. As far as our set of glasses is concerned, neither the  $\gamma$ -values of the semi-conductors Se-Ge nor those of electrolyte glass or vitreous silica scale against  $T_g$ . However, for any of the variables  $C_{11}$ ,  $C_{44}$ ,  $v_D$  or  $T_g$ , we observe an increase of the  $\gamma^2$ -values proportional to the stiffness of the material. Thus, we focus on the variation of  $\gamma_1^2$  and  $\gamma_t^2$  as functions of the relevant longitudinal and transverse elastic constants, which is shown in Fig. 3. For both of the polarizations the squared coupling constant increases proportionally to increasing  $C_{11}$  and  $C_{44}$ . We note that the main result in Fig. 3 concerns the transverse polarization, since transverse phonons dominate the average acoustic properties at low temperatures. It is also worthwhile noting that the different amorphous materials form groups of determined stiffness:  $C_{44} \approx 0.5 \cdot 10^{10} \text{N/m}^2$  is characteristic of polymers and semi-conductors, whereas covalent oxide glasses scale around  $C_{44} \approx 2 \dots 3 \cdot 10^{10} \text{N/m}^2$  (for lead- and fluorozirconate glasses) and  $C_{44} \approx 3 \dots 4 \cdot 10^{10} \text{N/m}^2$  (for silica, BK7 and LAT).

In order to search for correlations between  $\bar{P}$  and elastic bulk properties we further analysed the apparent constant slope  $\gamma_t^2/C_{44}$  in Fig. 3. The variation of  $\bar{P}$  vs.  $\gamma_t^2/C_{44}$  is shown in Fig. 4 where again the  $\bar{P}$ -data for

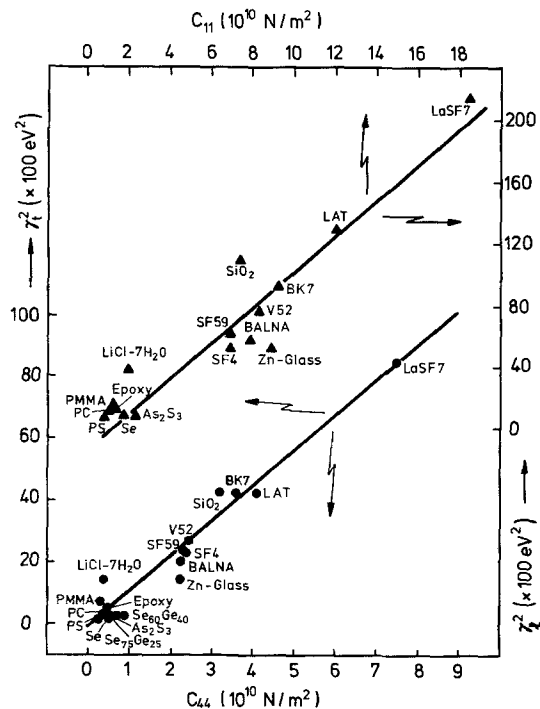


Fig. 3. Variation of the squared TLS-phonon coupling energy with elastic constants for longitudinal (upper) and transverse (lower) modes. The straight lines are a guide to the eye, only

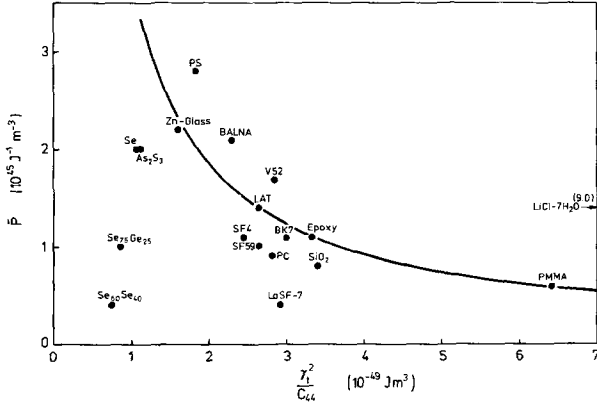


Fig. 4. Variation of the TLS spectral density  $\bar{P}$  with the ratio  $\gamma_i^2/C_{44}$ . The full line is calculated from eq. (7) according to an empirical relation reported by Freeman and Anderson [6]

the set of 18 glasses exhibit no uniform behaviour. With the exception of the semi-conducting glasses the data for the other glasses show the trend that with increasing  $\gamma_i^2/C_{44}$  the spectral density seems to decrease. A similar variation has been reported by Freeman and Anderson [6] from an analysis of thermal conductivity data. Below 1 K, the thermal conductivity of amorphous materials shows a universal behaviour according to  $k \propto T^n$  where  $n \approx 1.8-2.0$ . In the framework of the standard tunnelling model this result is explained by a phonon mean free path  $l = 1/\alpha$  as given by (2). Reviewing low temperature thermal conductivity data on a variety of glasses, Reynolds [23] and more recently Freeman and Anderson [6] have shown that an empirical relation  $l/\lambda \approx 150$ , where  $\lambda$  is the wavelength of dominant phonons, should be considered as a general feature of glasses. Using (2), this relation can be written

$$\lambda/l = f \cdot \bar{P} \cdot \frac{\gamma^2}{\rho \cdot v^2} \approx 1/150 \quad (7)$$

where  $f \approx 18$  (in the dominant phonon approximation) and  $v$  and  $\gamma$  are mode average quantities. As the transverse phonons dominate the low temperature elastic properties we estimate  $\gamma^2/(\rho \cdot v^2) \approx \gamma_i^2/C_{44}$ , and in Fig. 4 the resulting hyperbolic function is shown. We note that the data of the 4 amorphous polymers agree to (7) within a wide range of values whereas for the inorganic glasses less validity is found.

Some years ago, Klein et al. [12] pointed out that static strain interactions between TLS can cause a continuous energy distribution. According to this calculation the density of TLS scales proportionally to the quantity  $\tilde{C}/\gamma_i^2$  where  $\tilde{C} = (C_{44}^{-1} - C_{11}^{-1})^{-1}$ . In view of the agreement between the empirical relation (7) based on thermal conductivity data and the analysis presented here, we suggest to do further studies on a

dependence  $\bar{P}$  vs.  $\tilde{C}/\gamma_i^2$  in a wider range of  $\gamma_i^2/C_{44}$ -values. Within the ensemble of glasses presented here, the variation of  $C_{44}/\gamma_i^2$  is of a factor of  $\sim 5$  only, and therefore too small to provide clear evidence of this relationship.

Finally, we shall report on a remarkable behaviour related to the parameter  $K_3$  which is derived from absorption data. According to the tunnelling model a shortest relaxation time  $\tau_{\min}$  for a TLS exists, and in the dominant phonon approximation  $\tau_{\min}$  is given by [22]

$$\tau_{\min}^{-1} = 2 \cdot K_3 \cdot T^3. \quad (8)$$

In Fig. 5 we have plotted  $\tau_{\min}$  (calculated from Eq. (8) with  $T = 0.1$  K) against the glass transition temperature  $T_g$ . Contrary to the finding in Fig. 2, we observe a correlation between the relaxation of the tunnelling entities and the high temperature relaxational processes related to the glass formation. The increase of  $\tau_{\min}$  within two orders of magnitude is proportional to  $T_g^n$  with  $n \approx 2.5$ . For vitreous silica  $\tau_{\min}^{0.1K} = 1.2 \mu\text{s}$ , and for  $\text{LiCl} \cdot 7\text{H}_2\text{O}$   $\tau_{\min}^{0.1K} = 60$  ns; i.e. the higher the glass transition temperature, the higher the cut-off values  $\tau_{\min}$  of the TLS distribution function  $P(E, \tau)$ . In a simplified picture one can qualitatively interpret the above result: At the glass transition temperature, the constituents of a glass significantly change their positions via thermally activated processes against potential barriers of the order  $k_B T_g$ . On the other hand, with respect to the tunnelling model,  $\tau_{\min}$  is related to tunnelling systems originating from symmetric double well potentials where the tunnelling splitting energies are dependent on the shape of the barriers. Thus, if  $T_g$  is lower for a certain glass, the distribution of potential barriers is

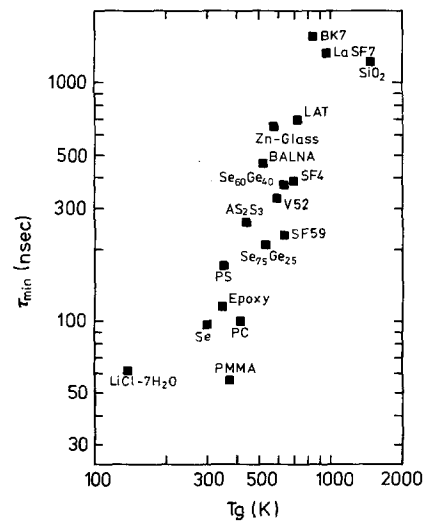


Fig. 5. Variation of the minimum TLS relaxation time  $\tau_{\min}$  (calculated at  $T = 0.1$  K from eq. (8)) with the glass transition temperature  $T_g$

shifted to lower energies resulting in shorter relaxation times. Since the TLS parameters  $\gamma_{1,t}$  and  $\bar{P}$  do not correlate with  $T_g$ , the  $\tau_{\min}$  dependence shown in Fig. 5 represents an interesting result which should be considered essential in further studies on the nature of TLS.

#### IV. Conclusion

The universal low temperature acoustic properties of glasses have been examined with a consistent analysis of absorption and dispersion data available below 1 K. For a large spectrum of amorphous solids, i.e. 8 oxide glasses, 4 semi-conductor glasses, 4 amorphous polymers, the non-magnetic Zn-glass and the electrolyte glass LiCl-7H<sub>2</sub>O, on the basis of the standard tunnelling model [13] we determined the TLS spectral density  $\bar{P}$  and the coupling constants  $\gamma_{1,t}$ . Contrary to reports [4, 5, 8–11] on a dependence of  $\bar{P}$  on the glass transition temperature  $T_g$  we do not find a significant variation of  $\bar{P}$  vs.  $T_g$  for this set of 18 glasses. Within the scattering of  $\bar{P}$ -values we notice that the TLS spectral densities remain in the range of  $\bar{P} = (0.5 \dots 2.5) \cdot 10^{45} \text{ J}^{-1} \text{ m}^{-3}$ . A trend  $\bar{P} \propto 1/T_g^n$  with  $n \approx 1-3$  is evident only for glasses of the same class, as defined by composition and chemical bonding.

With respect to the TLS coupling constants  $\gamma_1$  and  $\gamma_t$ , the elastic constants  $C_{11}$  and  $C_{44}$  appeared to be appropriate quantities for the correlation of TLS parameters and structural parameters of a glass. Despite the apparent scatter of  $\bar{P}$ -values within our set of 18 glasses, a relation  $\bar{P} \cdot \gamma_t^2 / C_{44} = \text{const.}$  seems to be possible. As well from an analysis of thermal conductivity data below 11 K [6] as from theoretical work on the static strain interaction between two-level systems [12] arguments can be provided for a variation  $\bar{P} \propto C_{44} / \gamma_t^2$ . For the present set of glasses both quantities vary only by a factor of  $\sim 5$  which is too small to prove such a dependence. More studies on amorphous materials with different ratios  $\gamma_t^2 / C_{44}$  are needed to clarify the underlying physical picture.

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#### References

1. For a General Review on Low Temperature Properties in Disordered Solids: Amorphous solids, Phillips, W.A. (ed.) Berlin, Heidelberg, New York: Springer 1981
2. Pohl, R.O., DeYoreo, J.J., Meißner, M., Knaak, W.: in Physics of

- disordered materials. p. 529. Adler, D., Fritzsche, M., Ovshinsky, S. (eds.), New York: Plenum Press 1985
3. Anderson, P.W., Halperin, B.I., Varma, C.M.: Philos. Mag. **25**, 1 (1972); Phillips, W.A.: J. Low Temp. Phys. **7**, 351 (1972)
4. Raychaudhuri, A.K., Pohl, R.O.: Solid State Commun. **37**, 105 (1980); Phys. Rev. B **25**, 1310 (1982)
5. MacDonald, W.M., Anderson, A.C., Schroeder, J.: Phys. Rev. B **31**, 1090 (1985)
6. Freeman, J.J., Anderson, A.C.: Phys. Rev. B **34**, 5684 (1986)
7. Graebner, J.E., Golding, B., Allen, L.C.: Phys. Rev. B **34**, 5696 (1986)
8. Doussineau, P., Matecki, M., Schön, W.: J. Phys. (Paris) **44**, 101 (1983)
9. Cohen, M.H., Grest, G.S.: Solid State Commun. **39**, 143 (1981)
10. Reichert, U., Schmidt, M., Hunklinger, S.: Solid State Commun. **57**, 315 (1986); Reichert, U.: Thesis, Universität Heidelberg 1986 (unpublished)
11. Hunklinger, S.: Quantum aspects of molecular motions in solids. In: Heidemann, A. et al. (eds.), Springer Proceedings in Physics, Vol. 17, p. 194. Berlin, Heidelberg, New York: Springer 1987
12. Klein, M.W., Fischer, B., Anderson, A.C., Anthony, P.J.: Phys. Rev. B **18**, 5887 (1978)
13. See e.g.: Hunklinger, S., Raychaudhuri, A.K.: In: Progress in low-temperature physics. Brewer, D.F. (ed.) Vol. IX, p. 265. Amsterdam: North-Holland 1986
14. A more complete set of disordered solids for which low temperature acoustic data are available in literature contains 35 elements. For more details, see: Berret, J.F.; These d'état, Université de Montpellier 1987 (unpublished)
15. Weiss, G., Hunklinger, S., Löhneysen, H. v.: Physica **109 + 110 B**, 1946 (1982)
16. BK-7: borosilicate crown of composition (wt.%) 69.9 SiO<sub>2</sub>, 9.9 B<sub>2</sub>O<sub>3</sub>, 8.4 NaO<sub>2</sub>, 8.4 K<sub>2</sub>O, 2.5 BaO; LaSF-7: dense lanthanum flint containing mostly B<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub> and ThO<sub>2</sub> with a few % Ta<sub>2</sub>O<sub>5</sub> and Nb<sub>2</sub>O<sub>5</sub>; SF4: alkali-lead silicate of composition (mol.%) 60.8 SiO<sub>2</sub>, 34.9 PbO, 2.5 K<sub>2</sub>O and 1.8 other; SF59: as SF4, but 35.3 SiO<sub>2</sub>, 55.6 PbO, 0.8 K<sub>2</sub>O, 7.9 B<sub>2</sub>O<sub>3</sub> and 0.4 other; V52: fluorozirconate of composition (wt.%) 57.5 ZrF<sub>4</sub>, 33.8 BaF<sub>2</sub> and 8.75 ThF<sub>4</sub>; BALNA: as V52, but 52 ZrF<sub>4</sub>, 24 BaF<sub>2</sub>, 4 AlF<sub>3</sub> and 20 NaF; LAT: as V52, but 60 ZrF<sub>4</sub>, 33 ThF<sub>4</sub> and 7 LaF<sub>3</sub>; Zn-glass: fluorophosphate (ZnF<sub>2</sub>)<sub>0.60</sub> (BaF<sub>2</sub>)<sub>0.20</sub> (NaPO<sub>3</sub>)<sub>0.20</sub>; PMMA: amorphous polymer polymethyl-metacrylate; PS: amorphous polymer polystyrene; PC: amorphous polymer polycarbonate; Epoxy: an epoxy resin produced by SILITRO, under reference ET 1000
17. Duquesne, J.Y., Bellessa, G.: Philos. Mag. **B 52**, 821 (1985)
18. For normal and superconducting metallic glasses this ratio is reduced to 1.6; see e.g.: Bellessa, G.: J. Phys. (Paris) **41**, C8-723 (1980)
19. Kasper, G., Röhring, V.: Proceedings of the 17th International Conference of Low Temperature Physics. Eckern, U., Schmid, A., Weber, W., Wühl, H. (eds.), p. 385. Amsterdam: North-Holland 1984.
20. The transverse velocity for LiCl-7H<sub>2</sub>O is derived by assuming the same value of the ratio  $v_t/v_l$  for electrolytes as well as for pure amorphous water; see: Hardle, H.: Thesis, Universität Heidelberg 1985 (unpublished)
21. Zeller, R.C., Pohl, R.O.: Phys. Rev. B **4**, 2029 (1971); see also Pohl, R.O.: In Ref. 1
22. Black, J.L.: Phys. Rev. B **17**, 2740 (1978)
23. Reynolds, C.L., J. Non-Cryst. Solids **30**, 371 (1979)

*Additional References:* a) Doremus, R.H.: Glass science. (New York: Wiley 1973); b) Ng, D., Sladek, R.J.: Phys. Rev. B **11**, 4017 (1975); Laermans, C., Piché, L., Arnold, W., Hunklinger, S.: in "Non-Crystalline Solids", Frischat, G.H. (ed.) Aerdernsdorf: Trans Tech 1977, p. 542; c) Sakka, S., Mackenzie, J.D.: J. Non-Cryst. Solids **6**, 145 (1971); d) Berret, J.F., Pelous, J., Vacher, R.,

Raychaudhuri, A.K., Schmidt, M.: *J. Non-Cryst. Solids* **87**, 70 (1986);  
e) Morr, W.: Diplomarbeit, Universität Heidelberg 1986 (unpublished);  
f) Sarrach, D.J., DeNeuville, J.P., Haworth, W.L.: *J. Non-Cryst. Solids* **22**, 245 (1976); g) Doussineau, P., Levelut, A., Matecki, M., Schön, W., Wallace, E.: *J. Phys* **46**, 979 (1985); h) Federle, G.: Thesis, Universität Konstanz 1983 (unpublished); i) Duquesne, J.Y., Bellessa, G.: *J. Phys (Paris) Lett* **40**, L193 (1979); j) Schön, W.: Thèse de 3ème Cycle, Université de Paris VI 1983 (unpublished)

J.F. Berret  
Laboratoire de Science des

Matériaux Vitreux  
Université de Montpellier II  
F-34060 Montpellier  
France

M. Meissner  
Hahn-Meitner-Institut  
Berlin GmbH  
Bereich Kernchemie und Reaktor  
-Neutronenstreuung II-  
Glienicke Strasse 100  
D-1000 Berlin 39  
Germany