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Ultrasonic propagation in a fluorozirconate glass from 0.08 K to 250 K

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Résumé. — L'atténuation et la variation de la vitesse de phase d'ondes ultrasonores longitudinales et transverses ont été mesurées dans le verre au tétrafluorure de zirconium de composition 57,5 % ZrF_4 , 33,75 % BaF_2 et 8,75 % ThF_4 , pour des températures allant de 0,08 K à 250 K. Le comportement habituel des verres isolants a été observé aux plus basses températures, révélant l'existence de systèmes à deux niveaux (S2N). De ces mesures ultrasonores, non seulement les constantes de couplage entre les S2N et une onde acoustique longitudinale et transverse ont été calculées mais aussi la densité d'états des S2N.

Abstract. — The attenuation and phase velocity variation of longitudinal and transverse ultrasonic waves have been measured in the fluorozirconate glass 57.5 % ZrF_4 , 33.75 % BaF_2 and 8.75 % ThF_4 , in the temperature range 0.08 to 250 K. The usual behaviour of amorphous insulators has been observed at the lowest temperatures indicating the existence of two-level tunnelling systems (TLS). From these acoustic measurements not only the coupling constants between TLS and longitudinal and transverse acoustic waves, but also the TLS density of states have been determined.

1. Introduction. — In the past decade some major advances have been obtained in the knowledge of the low temperature properties of amorphous materials. At temperatures lower than a few K it appears that practically all glasses, whether insulating [1] or metallic [2], have similar properties. Most of them are satisfactorily explained in the framework of the tunnelling model which postulates the existence of supplementary excitations characteristic of the amorphous state [3, 4]. These excitations are usually described by particles moving between two potential wells separated by an energy barrier. At low temperatures the movement of the particles only occurs *via* tunnelling through the energy barrier. This is a phenomenological model and the nature of the tunnelling particles is still unknown.

In order to gain some new information on these excitations, experiments in materials presenting similar behaviour, but in which the microscopic nature of the defects is known, have recently been performed. Among these materials are neutron irradiated quartz [5], smoky quartz [6], and doped β -alumina [7]. In this paper we present another way of approaching this

problem. We have studied a new class of materials. The fluorozirconate glasses were recently discovered [8]. They have some new and promising properties : they contain no oxygen and no tetrahedrally coordinated atoms ; their optical properties make them attractive materials as optical windows and good hosts for high-power lasers [9]. It is thought that the vitreous network is composed of ZrF_6 , ZrF_7 and ZrF_8 polyhedra. It is this difference in the structure as compared to the well studied silica-based glasses which is most interesting from the point of view of the low temperature properties.

In this letter we present the results of acoustic propagation experiments in a fluorozirconate glass in the temperature range 0.08 K to 250 K. Our results show the usual acoustic behaviour of amorphous insulators at low temperatures : i) the attenuation is higher at low intensity (saturation effect) ; ii) the high intensity attenuation increases first as $\omega^0 T^3$; iii) the phase velocity first increases as the logarithm of the temperature, passes through a maximum near 2 K and then decreases. All these features are in agreement with the two-level tunnelling systems (TLS) theory. From the measurements we are able to determine the coupling constants of the longitudinal and the transverse acoustic waves with the TLS *and* also the density of states of

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the TLS. For the first time the TLS density of states of an amorphous material is determined directly from ultrasonic experiments. Usually, this quantity is obtained from low temperature specific heat measurements.

2. Experiments. — 2.1 EXPERIMENTAL METHODS. —

The material used here was a ternary compound of the following composition : 57.5 % ZrF_4 , 33.75 % BaF_2 , 8.75 % ThF_4 [10]. It has been designated by the V 52 symbol in previous publications [9, 10]. Details of the preparation procedure have been given elsewhere [11]. The specific mass is $\rho = 4.8 \text{ g.cm}^{-3}$, and the glass temperature $T_G = 320 \text{ }^\circ\text{C}$. Various samples about 5 mm long were prepared from two different ingots for acoustic experiments. Standard pulse echo techniques were used. Within experimental accuracy all the samples gave the same results.

2.2 EXPERIMENTAL RESULTS. — The propagation velocity of the acoustic waves was first measured at 0.1 K. We found $v_L = 4.15 \times 10^5 \text{ cm.s}^{-1}$ and $v_T = 2.25 \times 10^5 \text{ cm.s}^{-1}$ for longitudinal and transverse polarizations respectively.

The results for the intensity dependence of the longitudinal wave attenuation at the frequency $\omega/2\pi = 745 \text{ MHz}$ are shown in figure 1 at two temperatures.

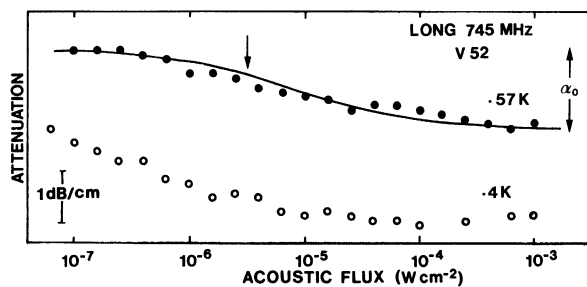


Fig. 1. — Attenuation as a function of the ultrasonic intensity for a longitudinal wave of frequency 745 MHz propagating in an amorphous V 52 sample, the composition of which is 57.5 % ZrF_4 , 33.75 % BaF_2 , 8.75 % ThF_4 . The solid line is a calculated curve of the form $\alpha = \alpha_0(1 + J/J_c)^{-1/2}$, with $\alpha_0 = 1.7 \text{ dB.cm}^{-1}$ and J_c (marked by the arrow) $\simeq 2 \times 10^{-6} \text{ W.cm}^{-2}$.

Clearly, there is a saturation effect, i.e. the attenuation is higher at low intensity. The effect increases when the temperature decreases. However, because the critical intensity between the high intensity and low intensity regimes is shifted towards lower values when the temperature decreases, we are not able to observe saturation effects at temperatures lower than 0.4 K.

The high intensity attenuation was measured as a function of the temperature at various frequencies. The results are shown in figures 2 and 3 for longitudinal and transverse waves respectively. Similar behaviour was observed for the two acoustic modes. At the lowest temperatures ($T < 0.8 \text{ K}$) there is a region where the attenuation for all frequencies falls on the

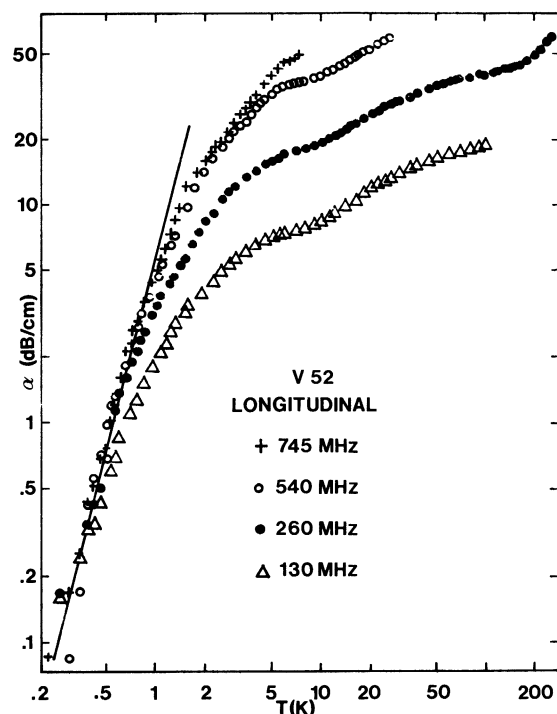


Fig. 2. — Ultrasonic attenuation as a function of the temperature in a log-log plot for various frequencies of a longitudinal wave propagating in an amorphous V 52 sample (57.5 % ZrF_4 , 33.75 % BaF_2 , 8.75 % ThF_4). The solid straight line has a slope 3.

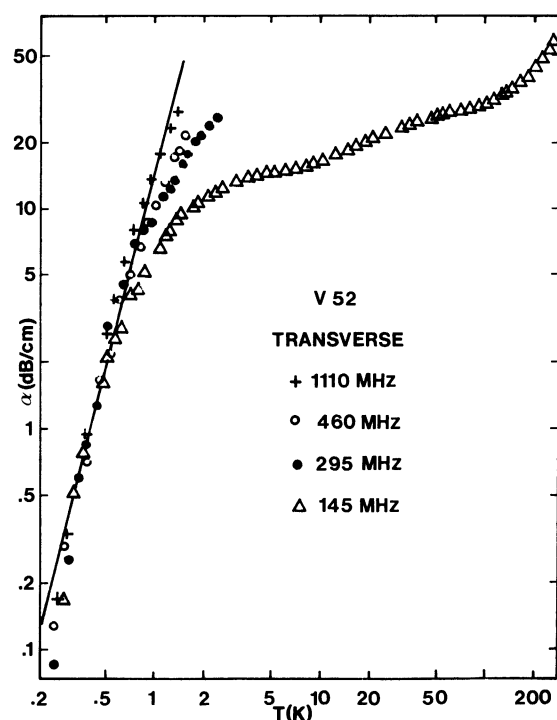


Fig. 3. — Ultrasonic attenuation as a function of the temperature in a log-log plot for various frequencies of a transverse wave propagating in a fluorozirconate glass V 52. The solid straight line has a slope 3.

same line within the experimental accuracy. The slope of this line is very close to 3, so that the attenuation is described in this temperature range by $\alpha \sim \omega^0 T^3$.

At higher temperatures the attenuation becomes frequency dependent following a linear law. The temperature dependence does not follow a simple law throughout the explored region.

The temperature dependence of the velocity was also measured at various frequencies for both longitudinal and transverse waves. The results are shown in figure 4 using semi-logarithmic coordinates. The velocity first increases as the logarithm of the temperature from 0.08 K to about 1 K, then goes through a maximum, the position of which is frequency dependent and lies near 2 K at the frequencies used. Finally, the velocity decreases when the temperature increases further.

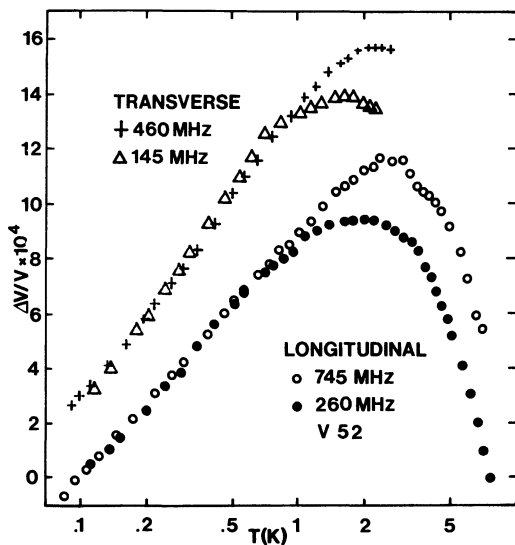


Fig. 4. — Phase velocity change of an ultrasonic wave propagating in a fluorozirconate glass V 52 (57.5 % ZrF₄, 33.75 % BaF₂, 8.75 % ThF₄) in a semi-log plot. Top : transverse polarization ; bottom : longitudinal polarization. The two sets of points are arbitrarily shifted one from the other.

3. Theory. — We interpret our results in terms of the TLS theory. The interaction of an ultrasonic wave of frequency $\omega/2\pi$ with a TLS of energy E leads to two different processes. In the resonant process a phonon of energy $\hbar\omega$ is absorbed resonantly by the TLS. The attenuation of the ultrasonic wave is given by [1] :

$$\alpha = \frac{1}{(1 + J/J_c)^{1/2}} \frac{\pi\omega}{v_\tau} C_\tau \tanh\left(\frac{\beta\hbar\omega}{2}\right) = \frac{\alpha_0}{(1 + J/J_c)^{1/2}} \quad (1)$$

where v_τ is the velocity of the acoustic wave, $\tau = L$ or T stands for the polarization, J is the acoustic intensity, J_c a critical value. $C = \bar{P}\gamma_\tau^2/\rho v_\tau^2$, where \bar{P} is the constant density of states of the TLS, γ_τ is a deformation potential, ρ is the specific mass of the material,

$\beta = 1/k_B T$. The corresponding velocity change is given in the case $\hbar\omega \ll kT$ by [1] :

$$\frac{\Delta v}{v} = C_\tau \ln(T/T_0) \quad (2)$$

where T_0 is an arbitrary reference temperature.

In the second process, the acoustic wave modulates the TLS splitting. The new thermal equilibrium takes place with a characteristic relaxation time T_1 . This process gives a relaxational attenuation which can be written as

$$\alpha = \frac{\omega^2 \bar{P}\gamma_\tau^2}{\rho v_\tau^3} \int_0^\infty d\left(\frac{\beta E}{2}\right) \operatorname{sech}^2 \frac{\beta E}{2} \times \int_{r_{\min}}^1 dr (1-r)^{1/2} r^{-1} \frac{T_1}{1 + \omega^2 T_1^2} \quad (3)$$

If the relaxation of the TLS occurs *via* the one-phonon (or direct) process T_1 is given by

$$T_1^{-1} = r K_3 T^3 \left(\frac{\beta E}{2}\right)^3 \coth \frac{\beta E}{2} \quad (4)$$

with

$$K_3 = \frac{4 k_B^3}{\pi \rho \hbar^4} \sum_\tau \frac{\gamma_\tau^2}{v_\tau^5} \quad (5)$$

In these formulae the distribution of the coupling constant is taken into account by the parameter $r = (\Delta_0/E)^2$, where Δ_0/\hbar is the tunnelling frequency, r varies between a minimum value r_{\min} and 1. As a consequence there is a distribution of the relaxation times T_1 . The minimum value (T_1^m) for T_1 is obtained by setting $r = 1$ in equation (4). Full details on this point can be found in reference [15].

The attenuation α as given by equation (3) has to be calculated by numerical integration. However the behaviour in the following limits can be obtained analytically [12] :

— if $\omega T_1^m \gg 1$ (low temperature regime)

$$\alpha = \frac{\pi^4}{96} C_\tau \frac{K_3}{v_\tau} T^3 \quad (6)$$

— if $\omega T_1^m \ll 1$ (high temperature regime)

$$\alpha = \frac{\pi\omega}{2 v_\tau} C_\tau \quad (7)$$

4. Discussion. — Clearly, our acoustic propagation results can be explained by the interaction of the TLS with the elastic wave. The logarithmic increase of the velocity below about 1 K is ascribed to the resonant interaction between the TLS and the elastic wave. From equation (2) we deduce $C_L = 4.2 \times 10^{-4}$ and $C_T = 4.7 \times 10^{-4}$.

The $\omega^0 T^3$ law of the attenuation in the temperature range 0.2-0.8 K is attributed to the relaxation of the

TLS by a one-phonon process in the case where $\omega T_1^m \gg 1$. Knowing C_L , C_T , v_L and v_T , we deduce from equation (6) two independent values for the parameter K_3 : 1.4×10^9 and $1.6 \times 10^9 \text{ K}^{-3} \cdot \text{s}^{-1}$, from the longitudinal and transverse attenuation, respectively.

From C_L , C_T and K_3 we deduce the values of the deformation potentials $\gamma_L = 0.95 \text{ eV}$ and $\gamma_T = 0.52 \text{ eV}$, and also the value of the TLS density of states $\bar{P} = 1.5 \times 10^{32} \text{ erg}^{-1} \cdot \text{cm}^{-3}$.

These three values are of the same order of magnitude as those measured in silica based glasses [1]. It would be interesting to perform specific heat experiments on this material in order to determine in a different way the TLS density of states. However two points must be kept in mind: first, in a specific heat experiment the total density of states of all the excitations is measured; secondly the quantities determined from an ultrasonic experiment are in fact averages which are not necessarily the same for the resonant or the relaxational contributions. Therefore a precise comparison is difficult.

With the above value of K_3 an estimate of T_1^m can be made. At 0.57 K for $\omega/2\pi = 745 \text{ MHz}$, we find $T_1^m = 3.5 \mu\text{s}$.

With equation (1) the resonant attenuation can be calculated. For longitudinal wave of frequency 745 MHz at 0.57 K we deduce $\alpha_0 = 2 \text{ dB} \cdot \text{cm}^{-1}$ which compares well with the value $\alpha_0 = 1.7 \text{ dB} \cdot \text{cm}^{-1}$ from the saturation experiment (see figure 1). An estimate of the critical intensity J_c can be also obtained. In the same conditions (745 MHz, 0.57 K)

$$J_c \sim 10^{-6} \text{ W} \cdot \text{cm}^{-2}.$$

The critical intensity is given by

$$J_c = \frac{\rho v^3 \hbar^2}{2 \gamma^2 \Delta t T_2},$$

where T_2 is the transverse relaxation time of the TLS, Δt is the width of the acoustic impulsion (we use Δt rather than T_1 because in our conditions $\Delta t < T_1$) with $\Delta t \simeq 0.6 \mu\text{s}$, an estimate of T_2 is obtained. $T_2 \sim 2 \times 10^{-8} \text{ s}$. These values of T_1 and T_2 are too

short to observe pseudo-spin ultrasonic echoes [13] at these temperatures.

The TLS theory predicts that at high temperatures the attenuation is independent of T and varies linearly with ω (Eq. (7)). Such a plateau has already been observed in $\alpha\text{-As}_2\text{S}_3$ [14] and also in $\text{Na-}\beta\text{-Al}_2\text{O}_3$ [15], but is clearly not seen in the fluorozirconate glass. Probably it is obscured by the low temperature side of the attenuation due to a process active at high temperature. The shoulder in the attenuation curves around 5-10 K (see figures 2 and 3) perhaps indicates the occurrence of this plateau. The linear ω law is well obeyed in this region and the expected attenuation ($23 \text{ dB} \cdot \text{cm}^{-1}$ at 540 MHz) is compatible with the measured attenuation. A complete description of the effects of the attenuation (and also of the velocity) in this temperature range needs much more work.

One must note that in amorphous materials an attenuation peak is usually observed near 50 K. In the fluorozirconate glass no attenuation peak has been observed up to 250 K. On the other hand attenuation curves similar to those presented here have already been observed in some amorphous materials like B_2O_3 [16] and sodium phosphate glasses [17].

5. Conclusion. — From our low temperature measurements of the attenuation and of the phase velocity change of both longitudinal and transverse acoustic waves in a fluorozirconate glass we have determined not only the longitudinal and transverse coupling constants between the elastic waves and the TLS but also the density of states of the TLS. The numerical values are of the same order of magnitude as those obtained from silica-based glasses although the microscopic nature of the materials are different. However the acoustic behaviour at relatively high temperatures ($T > 5 \text{ K}$) is different in the two materials.

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References

- [1] HUNKLINGER, S. and ARNOLD, W., in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic Press, N. Y.) 1976, vol. XII, p. 155.
- [2] BLACK, J. L., in *Metallic Glasses*, edited by H. J. Güntherodt (Springer Verlag, N. Y.) 1980, to be published.
- [3] PHILLIPS, W. A., *J. Low Temp. Phys.* **7** (1972) 351.
- [4] ANDERSON, P. W., HALPERIN, B. I. and VARMA, C. M., *Philos. Mag.* **25** (1972) 1.
- [5] LAERMANS, C., *Phys. Rev. Lett.* **42** (1979) 250.
- [6] CHAUSSY, J., GILCHRIST, J. LE G., LASJAUNIAS, J.-C., SAINT-PAUL, M. and NAVA, R., *J. Phys. Chem. Solids* **40** (1979) 1073.
- [7] ANDERSON, A. C., in *Fast Ion Transport in Solids*, edited by P. Vashishta, J. N. Mundy and G. K. Shenoy (North-Holland) 1979, p. 255.
- [8] POULAIN, M., POULAIN, M., LUCAS, J. and BRUN, P., *Mat. Res. Bull.* **10** (1975) 242.
- [9] POULAIN, M. and LUCAS, J., *Verres Refract.* **32** (1978) 505.
- [10] POULAIN, M., CHANTANASINH, M. and LUCAS, J., *Mat. Res. Bull.* **12** (1977) 152.
- [11] POULAIN, M., POULAIN, M. and LUCAS, J., *Brevet A.N.V.A.R.* n° 77.09618.
- [12] JÄCKLE, J., *Z. Phys.* **257** (1972) 212.
- [13] GOLDING, B. and GRAEBNER, J. E., *Phys. Rev. Lett.* **37** (1976) 852.
- [14] NG, D. and SLADEK, R. J., *Phys. Rev. B* **11** (1975) 4017.
- [15] DOUSSINEAU, P., FRÉNOIS, Ch., LEISURE, R. G., LEVELUT, A. and PRIEUR, J.-Y., *J. Physique* **41** (1980) 1193.
- [16] PELOUS, J., *Phys. Lett.* **74 A** (1979) 275.
- [17] PELOUS, J., VACHER, R. and PHALIPPOU, J., *J. Non-Cryst. Solids* **30** (1979) 385.