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Acoustic propagation in an epoxy resin at very low temperatures

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Résumé. — L'atténuation et la variation de vitesse d'ondes ultrasonores de fréquences jusqu'à 2,14 GHz ont été mesurées dans une résine époxy dans le domaine de température 0,1 à 80 K. Aux plus basses températures ($T \lesssim 0,8$ K) l'atténuation varie comme le cube de la température et est indépendante de la fréquence comme le prévoit la théorie standard des systèmes à deux niveaux. L'ensemble de nos résultats est discuté dans le cadre de cette théorie.

Abstract. — Attenuation and velocity changes of ultrasonic waves of frequencies up to 2.14 GHz have been measured in an epoxy resin in the temperature range 0.1 to 80 K. At the lowest temperatures ($T \lesssim 0.8$ K) the attenuation varies as the cube of the temperature and is frequency independent, as predicted by the standard TLS theory. All of our results are discussed in the framework of this theory.

1. **Introduction.** — Amorphous materials have low temperature properties quite different from those observed in crystals. Their specific heat contains an excess below about 1 K which varies linearly with the temperature T . Their phonon thermal conductivity varies as T^2 . Their acoustic behaviour is also quite characteristic: the velocity first increases logarithmically with temperature and the absorption is saturable. All these properties are believed to be intrinsic to the amorphous state. They have been observed in insulating glasses [1]. In amorphous metals the observed behaviour is similar; the main differences can be attributed to the presence of conduction electrons [2]. Most of the low temperature properties of semiconducting glasses and also amorphous polymers are similar to those of insulating glasses [1]. All these particular features are well explained in the framework of the two-level system (TLS) theory which assumes the existence of a particle moving in a double-well potential by quantum-mechanical tunnelling [1]. The TLS theory predicts that TLS and an acoustic wave interact *via* two different processes. In the first mechanism phonons of energy $\hbar\omega$ are resonantly absorbed by the TLS of energy splitting $E = \hbar\omega$. In the second

mechanism the modulation of the TLS splittings by the acoustic wave induces relaxation effects and then finally acoustic absorption. When the relaxation is due to absorption or emission of one thermal phonon (as is the case in insulators) the acoustic attenuation varies as $\omega^0 T^3$ at low temperatures ($T \lesssim 1$ K); at higher temperatures it varies as ωT^0 , independently of the relaxation process [3]. The change between the two regimes arises at a temperature which depends on the frequency. This behaviour has been observed in several amorphous insulators or disordered solids especially the T^3 law [1, 4]. In amorphous polymers the situation is somewhat different. As predicted by the TLS theory the resonant absorption has been observed in amorphous polymethylmethacrylate (PMMA) by Brillouin scattering [5] and the logarithmic temperature increase of the velocity in several amorphous polymers [5-8]. But the temperature and frequency dependences of the acoustic absorption in the 1 K range in amorphous polymers is unexpected. The attenuation can be well described by a ωT law in the 100 MHz range near 1 K in selenium [9] and polystyrene (PS) [6]. Moreover Brillouin scattering experiments in PMMA and polycarbonate (PC) have revealed a linear behaviour of the attenuation of 18 GHz acoustic waves in the 2 to 10 K range [5]. A question arises concerning the possible existence of a new relaxation mechanism

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for the TLS in polymers. For this reason we have performed ultrasonic experiments in an amorphous epoxy resin down to lower temperatures (0.1 K) and up to higher frequencies (up to 2.14 GHz) than in previous ultrasonic work. Under these conditions we can expect to observe the T^3 law of the absorption because this regime is reached more easily at low temperature and high frequency. Our results show that the behaviour predicted by the standard TLS theory for amorphous insulators is indeed observed in the epoxy resin. A preliminary account of this work has been published previously [10].

2. Samples and experimental methods. — Samples of commercial epoxy resin [11] of length 2.14 mm and section $4 \times 4 \text{ mm}^2$ were prepared with two flat and parallel faces. The density is 1.2 g.cm^{-3} . Because epoxy resin is a rather soft material, acoustic propagation experiments in this material are somewhat difficult. We have obtained the best results by bonding the sample with a silicone oil on a quartz delay line. For the present our results are restricted to longitudinal waves. The method used for the attenuation and phase velocity measurements was a standard pulse echo technique. First we have measured the velocity of longitudinal acoustic waves. At 0.1 K we have found $v_L = 3.25 \times 10^5 \text{ cm.s}^{-1}$. This value is in agreement with previous determinations in other epoxy resins [5, 12].

The low temperatures were obtained with a dilution refrigerator for the range 0.1 K to 1.5 K and with an He^3 refrigerator for the range 0.8 K to 80 K. We have verified that the agreement of the two sets of measurements is very good in the common temperature domain covered by the two refrigerators.

3. Experimental results. — The results of the attenuation measurements of acoustic longitudinal waves

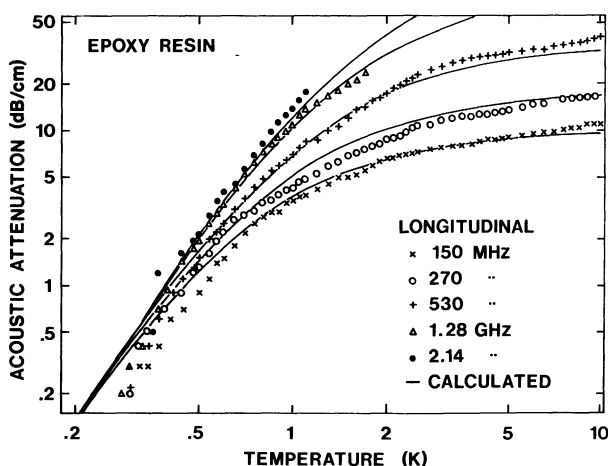


Fig. 1. — Temperature-dependent part of the attenuation of longitudinal acoustic waves propagating in an amorphous epoxy resin as a function of the temperature on a Log-Log scale for five frequencies. Solid lines are calculated taking into account only the direct process in the relaxational part of the attenuation.

in epoxy resin are presented in figure 1 in a Log-Log plot for five different frequencies ranging from 150 MHz to 2.14 GHz for the temperature range 0.1 K to 10 K. The main features are the following :

— at the lowest temperatures ($T \lesssim 0.8 \text{ K}$) there is a region where the attenuation falls on the same line within the experimental accuracy (except for the lowest frequency). The slope of this line is very close to 3, so that the dependence on the frequency and temperature is described by $\alpha \sim \omega^0 T^3$;

— at higher temperatures the attenuation becomes frequency dependent. This feature is seen more clearly in figure 2 where the data are plotted on a linear scale. They are restricted to the three lowest frequencies as a consequence of the large attenuation at the highest frequencies;

— at a temperature close to 3 K, which is in fact frequency dependent, there is a marked change of the slope of the attenuation as a function of the temperature (see Fig. 2);

— from about 4 K up to the highest temperature reached in our experiment (80 K) the attenuation increases monotonically (see Fig. 3).

At the lowest temperatures (below 1 K) we have searched for an intensity dependence of the attenuation. Upon varying the acoustic intensity by about 20 dB, no variation of the attenuation was detected. On the other hand we have observed an $\omega^0 T^3$ law. Therefore we conclude we have measured the high intensity (or saturated) part.

The results of the measurements of phase velocity changes are shown in figure 4 for two different frequencies on a semi-log plot. The behaviour is quite characteristic of an amorphous material. First the velocity increases as the logarithm of the temperature with a slope which is frequency independent, passing through a maximum and then decreasing with a quasi-linear temperature dependence (see Fig. 5).

4. Theory. — We interpret our results in the framework of the TLS theory. As mentioned in the introduction, an ultrasonic wave of frequency $\omega/2\pi$ interacts with a TLS *via* two different processes. In the resonant process a phonon of energy $\hbar\omega$ is absorbed resonantly by the TLS. This results in an attenuation and also a velocity change of the ultrasonic wave. This velocity change is given in the case $\hbar\omega \ll kT$ by [4] :

$$\frac{\Delta v}{v} = C \ln(T/T_0) \quad (1)$$

where T_0 is an arbitrary reference temperature. $C = \bar{P}\gamma^2/\rho v^2$ where \bar{P} is the spectral density of the TLS [13], and γ is a deformation potential which characterizes the phonon-TLS coupling.

In this paper we do not deal with the resonant absorption because it is observable only at low acoustic intensities not reached in our experiment.

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 leads to a relaxational attenuation which can be written as [3, 14] :

$$\alpha = \frac{\omega^2 C}{v} \int_0^\infty d\left(\frac{\beta E}{2}\right) \operatorname{sech}^2 \frac{\beta E}{2} \times \int_{r_{\min}}^1 dr (1-r)^{1/2} r^{-1} \frac{T_1}{1 + \omega^2 T_1^2}. \quad (2)$$

The corresponding velocity change is given by :

$$\frac{\Delta v}{v} = C \int_0^\infty d\left(\frac{\beta E}{2}\right) \operatorname{sech}^2 \frac{\beta E}{2} \times \int_{r_{\min}}^1 dr (1-r)^{1/2} r^{-1} \frac{1}{1 + \omega^2 T_1^2}. \quad (3)$$

If the relaxation of the TLS occurs *via* the one-phonon process, T_1 is given by [3] :

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

with

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

where $\beta = 1/k_B T$ and $\tau = L$ or T (longitudinal or transverse). In these formulae the distribution of the coupling constants is taken into account by the parameter $r = (\Delta_0/E)^2$ where Δ_0/\hbar is the tunnelling frequency. As a consequence there is a distribution of the relaxation times T_1 . By setting $r = 1$ in equation (4) the minimum value (T_1^m) for T_1 is obtained. The integral over r in equations (2) and (3) is calculated analytically and the integral over E is calculated numerically. However the attenuation and the velocity can be obtained exactly in the following limits :

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

$$\alpha = \frac{\pi^4}{96} C \frac{K_3}{v} T^3 \quad (5)$$

$$\frac{\Delta v}{v} = - \frac{\pi^6}{315} \frac{CK_3^2 T^6}{\omega^2}; \quad (6)$$

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

$$\alpha = \frac{\pi}{2v} \omega C \quad (7)$$

$$\frac{\Delta v}{v} = \frac{C}{2} \ln \frac{\omega}{\omega_0} - \frac{3C}{2} \ln \frac{T}{T_0}, \quad (8)$$

where $\omega_0/2\pi$ and T_0 are arbitrary frequency and temperature references.

5. Discussion. — The first result of our experiments is a qualitative one : the observation of a $\omega^0 T^3$ law for

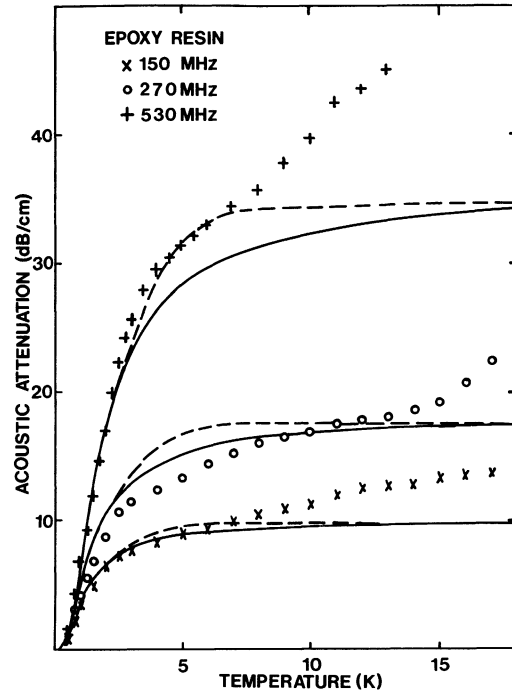


Fig. 2. — Same as figure 1 with a linear-linear scale but for only the three lowest frequencies. Solid lines have the same meaning as in figure 1. Dashed lines are calculated taking into account the direct plus the Raman process.

the acoustic attenuation at low temperature in an epoxy resin shows unambiguously that this amorphous polymer behaves in exactly the same manner as the usual insulating glasses such as silica, for example. Therefore there is no need to introduce a new relaxation mechanism for the TLS, specifically for the glassy polymers. Although the structure and the bonding in polymers are quite different from those of silica-based glasses, the low-temperature behaviour, which is a consequence of the existence of TLS, is the same in the two types of glasses.

The marked change of slope of the $\alpha(T)$ curves near 3 K (see Fig. 2) could be interpreted as the occurrence of the plateau of the attenuation (Eq. 7). But at temperatures above 3 K the attenuation still increases with the temperature. Therefore it is difficult to say if the plateau is indeed observed.

In order to test the TLS theory in detail we have calculated the acoustic attenuation and velocity change over all the temperature range from 0.1 K up to 30 K, using equations (2) and (4).

5.1 ATTENUATION. — The following procedure was used. First we attempted to obtain good agreement between calculated and experimental values for the attenuation. C and K_3 in equations (2) and (3) were taken as adjustable parameters (ρ and v_L were given in part 2). It was possible to obtain a very good fit for the lowest temperatures ($T \lesssim 3$ K) using the same values of $C = 5 \times 10^{-4}$ and $K_3 = 2.4 \times 10^9 \text{ K}^{-3} \cdot \text{s}^{-1}$ for all the five frequencies (see the solid lines in Fig. 1 and 2).

At higher temperatures ($T \gtrsim 3$ K) the agreement is not very good as can be seen on the linear plot of figure 2. In a second step of our procedure we tried to improve the fit by introducing a supplementary relaxation mechanism : the so-called Raman process in which the return to equilibrium of the perturbed TLS population occurs *via* the interaction with two thermal phonons [14]. As shown in detail in reference [14], the corresponding relaxation time is given by :

$$\frac{1}{T_1^R} = rK_7 T^7 F_7(\beta E) \quad (9)$$

with

$$K_7 = \frac{k_B^7}{\pi^3 \hbar^7} \sum_{\tau, \sigma} \frac{\delta_{\tau, \sigma}^2}{(\rho v_\tau^5)(\rho v_\sigma^5)} \quad (10)$$

τ and σ stand for the polarizations, δ is the coupling constant for this TLS-phonon interaction process, and

$$F_7(u) = \frac{u}{70} (u^2 + \pi^2) \left(u^4 - \pi^2 u^2 + \frac{10}{3} \pi^4 \right) \coth u. \quad (11)$$

The effective relaxation time of one TLS is given by

$$\frac{1}{T_1} = \frac{1}{T_1^D} + \frac{1}{T_1^R}. \quad (12)$$

With the Raman process, using $K_7 = 5 \times 10^3 \text{ K}^{-7} \cdot \text{s}^{-1}$ the fit is improved for the 530 MHz curve up to about 7 K. But, in fact, it was rather worse for the 270 MHz and 150 MHz curves. The results are given by the dashed lines in figure 2. Therefore the Raman process is not sufficient to explain all the acoustic attenuation in the epoxy resin.

As a temporary conclusion, it appears that the TLS theory, *via* the relaxational attenuation, gives a very good description of the acoustic attenuation in the epoxy resin below about 3 K. Above 3 K another

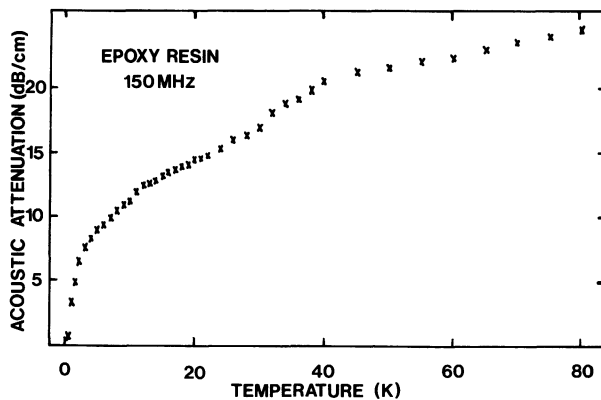


Fig. 3. — Temperature-dependent part of the attenuation of longitudinal acoustic waves propagating in an amorphous epoxy resin as a function of the temperature for the lowest frequency.

attenuation contribution arises, which is presently unidentified.

In most of the glasses [4] studied up to now (and especially in glassy polymers [9]) the acoustic attenuation at intermediate temperatures (from about 10 K to 100 K) is characterized by a peak. This peak is usually interpreted as the consequence of a thermally activated process (Arrhenius process) with a broad spectrum of the activation energies. We do not consider this process here because we have not observed such a peak in our measurements in the epoxy resin up to 80 K. In fact it is possible that the peak occurs at higher temperatures. And the excess of attenuation above 3 K can be interpreted as the low temperature side of an Arrhenius peak.

5.2 VELOCITY. — Now we turn to the discussion of the velocity changes. Besides the relaxational contribution to the velocity as given by equation (3) we have to take into account the resonant contribution given by equation (1) which cannot be saturated.

Immediately a first difficulty appears. It is necessary to use for the coefficient C , which is in front of equation (1), a value C_R which is different and lower than the value C inferred from the relaxational attenuation (Eq. 2). This problem was encountered previously in the disordered material $\text{Na-}\beta\text{Al}_2\text{O}_3$ [14]. It is in contradiction with the TLS model, at least in its standard version. In [14] a modified TLS distribution function has been proposed in order to take into account this experimental finding. In the following we use simply two values : C_R for the resonant process and C for the relaxational process. From the logarithmic increase of the velocity between 0.1 K and about

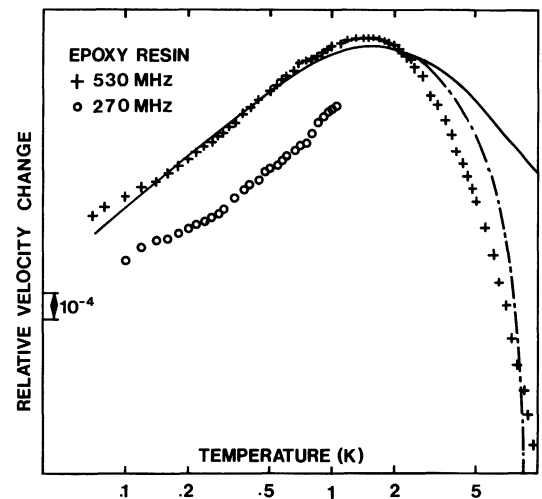


Fig. 4. — Semi-log plot of the relative phase velocity of 530 MHz longitudinal acoustic waves propagating in an amorphous epoxy resin as a function of the temperature. The solid line is calculated taking into account the resonant part and the relaxational part with only the direct process. The dot-dashed line is a calculated curve including a resonant contribution, a relaxational contribution (only direct process) plus an anharmonic term as explained in detail in the text.

1 K we found $C_R = 2.8 \times 10^{-4}$. We then calculated the velocity change with equations (3) and (4), using the same values $C = 5 \times 10^{-4}$, $K = 2.4 \times 10^9 \text{ K}^{-3} \cdot \text{s}^{-1}$ as for the attenuation and adding the resonant contribution (Eq. 1) with $C_R = 2.8 \times 10^{-4}$. The result is shown by the solid lines in figures 4 and 5. Obviously the fit is very bad above 3 K.

As for the attenuation we have tried to improve the fit by adding a Raman process for the relaxation of the TLS. Using the same value $K_7 = 5 \times 10^3 \text{ K}^{-7} \cdot \text{s}^{-1}$ as above, we have obtained the dashed line in figure 5. It cannot be said that the fit is really better !

It appears that above about 3 K most of the acoustic velocity change in the epoxy resin cannot be attributed to the TLS-phonon interaction, at least in terms of the presently known interaction processes. Therefore we have tried to interpret the observed velocity change as a consequence of the phonon-phonon interaction (or anharmonic process). In this case the velocity change can be written [15]

$$\left(\frac{\Delta v}{v}\right)_{\text{anh}} = -\frac{\gamma_G^2 C_v T}{\rho v^2} \quad (13)$$

where γ_G is an average Grüneisen constant and C_v is the Debye specific heat given by

$$C_v = 9 N k_B \left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2} \quad (14)$$

with θ the Debye temperature, $x_D = \theta/T$ and N is the number of acoustic modes. This contribution gives, at low temperatures, a T^4 variation ($C_v \propto T^3$) and at high temperature a linear T variation for the velocity. θ and γ_G were taken as free parameters. The dot-dashed lines in figures 4 and 5 show the result of the calculation taking into account the resonant and relaxational contributions with the coefficients C_R , C and K_3 as above and the anharmonic contribution with $\gamma_G = 10$ and $\theta = 150 \text{ K}$ (which corresponds to $N = 0.22 \times 10^{23} \text{ cm}^{-3}$). The fit is certainly better. But the calculated curve varies more rapidly with the temperature than the experimental curve. It is possible to obtain a better fit but in that case the value of θ becomes unphysically small. It can be also mentioned that the value of γ_G used here for the epoxy resin is high as compared to the values usually found in crystalline materials [15].

As a conclusion of this discussion of the velocity results, we cannot rule out the presence of an anharmonic term in the acoustic velocity variation but another presently unidentified term (related to the unidentified term of the attenuation ?) probably exists. However at the lowest temperatures ($T \lesssim 3 \text{ K}$) the velocity variation is well described in the framework of the TLS model.

5.3 TWO-LEVEL SYSTEMS IN THE EPOXY RESIN. — Now we will discuss our results in comparison with other work on glassy polymers. First from the values

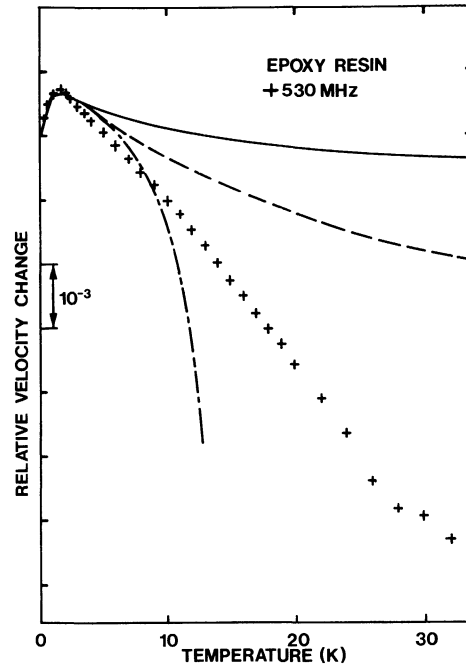


Fig. 5. — Same as figure 4 with a linear plot. The solid and dot-dashed lines have the same meaning as in figure 4. The dashed line is calculated including the resonant part plus the relaxational part in which two processes (direct and Raman) have been taken into account.

of C and K_3 , if we suppose $\gamma_L^2 \simeq 2 \gamma_T^2$ as for most of the amorphous insulators [4] and with $v_T = 1.6 \times 10^5 \text{ cm} \cdot \text{s}^{-1}$ [8, 12] we can deduce the TLS spectral density $\bar{P} \simeq 5.4 \times 10^{32} \text{ erg}^{-1} \cdot \text{cm}^{-3}$ and the TLS-phonon coupling constant $\gamma_L \simeq 0.2 \text{ eV}$. These values can be compared to the TLS density of states deduced from specific heat experiments ($1.3 \times 10^{33} \text{ erg}^{-1} \cdot \text{cm}^{-3}$ [12], and 1.6 and $1.1 \times 10^{33} \text{ erg}^{-1} \cdot \text{cm}^{-3}$ for two different epoxy resins [8]). The agreement can be considered good, if we take into account our assumptions in the determination of \bar{P} and the fact that usually \bar{P} is about one order of magnitude smaller than the density of states. The same authors, from their thermal conductivity experiments, have found for γ , values between 0.12 eV and 0.4 eV .

Now if we compare our results to other ultrasonic work, we note that our value $C_R = 2.8 \times 10^{-4}$ for epoxy resin is very close to the value 3.9×10^{-4} reported for PS [6] and to the value 5.1×10^{-4} for PMMA in a Brillouin scattering experiment [5].

Finally we were informed as this paper was being written that similar results have been obtained in other glassy polymers [16]. In glassy PMMA, PEMA (polyethylmethacrylate) and PC, Federler and Hunklinger have observed an $\omega^0 T^3$ law below about 0.2 K for ultrasonic frequencies up to 410 MHz . Also they mention that C_R is different to C . These results added to those presented here confirm the generality of the T^3 law in glassy polymers.

6. **Conclusion.** — The measurement of the attenuation of high frequencies ultrasonic waves down to 0.1 K in an epoxy resin has permitted us to observe for the first time in a polymer the $\omega^0 T^3$ law usually found in amorphous insulators. Therefore we have concluded that the standard TLS theory can be

applied to the amorphous polymers. A more detailed discussion has confirmed the agreement of the predictions of the TLS theory with our results up to about 3 K. At higher temperatures some presently unidentified mechanisms seem to play a dominant role.

References

- [1] See collected papers in *Amorphous Solids*, edited by W. A. Phillips (Springer Verlag) 1981.
- [2] BLACK, J. L., in *Metallic Glasses*, edited by H. J. Güntherodt and H. Beck (Springer Verlag) 1981, p. 167.
- [3] JÄCKLE, J., *Z. Phys.* **257** (1972) 212.
- [4] HUNKLINGER, S. and ARNOLD, W., in *Physical Acoustics*, edited by R. N. Thurston and W. P. Mason, vol. 12 (Academic Press) 1976, p. 155.
- [5] VACHER, R., PELOUS, J., SUSSNER, H., SCHMIDT, M. and HUNKLINGER, S., in *Proceedings of the E.P.S. Conference, Anvers* (1980).
- [6] DUQUESNE, J. Y. and BELLESSA, G., *J. Physique-Lett.* **40** (1979) L-193.
- [7] BELLESSA, G., LEMERCIER, C. and CALDEMAISON, P., *Phys. Lett. A* **62** (1977) 127.
- [8] MATSUMOTO, D. S., REYNOLDS, Jr, C. L. and ANDERSON, A. C., *Phys. Rev. B* **19** (1979) 4277.
- [9] DUQUESNE, J. Y. and BELLESSA, G., *J. Phys. C* **13** (1980) L-215.
- [10] DOUSSINEAU, P. and SCHÖN, W., in *Proceedings of the 5th International Conference « The Physics of Non-Crystalline Solids », Montpellier* (1982) to be published in *J. Physique Colloq.*
- [11] ET 1000 from Silitro Company.
- [12] KELHAM, S. and ROSENBERG, H. M., *J. Phys. C* **14** (1981) 1737.
- [13] In order to avoid confusion we propose to call \bar{P} the TLS spectral density. In the standard TLS theory \bar{P} is related to the actual TLS density of states $n(E)$ as measured by specific heat experiments by
- $$n(E) = \bar{P} \cosh^{-1} \left(\frac{E}{2A_m} \right) \approx \bar{P} \ln \frac{E}{A_m}$$
- where A_m is the minimum tunnelling energy.
- [14] We use here the notations of DOUSSINEAU, P., FRENOIS, C., LEISURE, R. G., LEVELUT, A. and PRIEUR, J.-Y., *J. Physique* **41** (1980) 1193.
- [15] See for example TRUPELL, R., ELBAUM, C. and CHICK, B. B., *Ultrasonic Methods in Solid State Physics* (Academic Press) 1969, p. 307, where the corresponding attenuation is derived. The order of magnitude of this attenuation is 1 dB/cm at high temperature (50 K) and at 150 MHz, and varies as ω^2 . Consequently we did not consider it in our calculation of the attenuation.
- [16] FEDERLE, G. and HUNKLINGER, S., in *Proceedings of the 5th International Conference « The Physics of Non-Crystalline Solids » Montpellier* (1982) to be published in *J. Physique Colloq.*