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Amorphous-like acoustical properties of Na doped $\beta$-Al$_2$O$_3$ (*)

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Résumé. — L’atténuation et la variation de la vitesse ultrasonores ont été mesurées dans l’alumine $\beta$ dopée au sodium sur une grande gamme de températures (1,7-80 K) et de fréquences (0,5-2 GHz). Les trois modes propres se propagent perpendiculairement à l’axe hexagonal ont été étudiés. Aux plus basses températures ($T \leq 10$ K) l’atténuation des trois modes est indépendante de la fréquence et varie comme le cube de la température. À plus haute température, l’atténuation devient indépendante de $T$: elle présente un plateau dont la hauteur est proportionnelle à la fréquence. Les vitesses de phase du mode longitudinal et du mode transverse polarisé perpendiculairement à l’axe $c$ croissent logarithmiquement en fonction de $T$, passent par un maximum aux alentours de 8 K puis décroissent quasi-linéairement. Pour l’autre mode transverse, le comportement de la vitesse est plus complexe. Tous ces résultats expérimentaux, et en particulier les variations de vitesse à l’exception de celle d’un mode, sont interprétés dans le cadre de la théorie des systèmes à deux niveaux développée pour les matériaux amorphes. La variation logarithmique en température de la vitesse et la loi en $T^3$ pour l’atténuation sont des résultats prévus et couramment observés dans les isolants amorphes. La mise en évidence d’un plateau pour l’atténuation est plus rare. Les conséquences de cette existence sont examinées: elle entraîne des conditions sur la forme de la fonction de distribution des systèmes à deux niveaux et elle prouve qu’il y a une distribution de l’intensité du couplage entre ces systèmes d’énergie donnée et les déformations élastiques.

Pour rendre compte des variations de l’atténuation dans la région au-dessus de 10 K, le processus direct de relaxation des systèmes à deux niveaux ne conduit pas à un accroissement suffisamment rapide en température. L’introduction d’un processus Raman donne la dépendance correcte en température. Enfin, pour la vitesse de phase, la dépendance quasi linéaire en température observée expérimentalement est bien reproduite si une contribution en $T^4$, due aux anharmonicités élastiques est ajoutée aux effets de la relaxation Raman. La théorie des systèmes à deux niveaux élaborée pour les matériaux amorphes explique donc l’ensemble des propriétés acoustiques (atténuation et vitesse de phase) de l’alumine $\beta$ dopée au sodium jusqu’à une température de 70 K. Par ailleurs, cette expérience confirme l’adéquation de la théorie des systèmes à deux niveaux pour rendre compte non seulement des effets résonnants mais aussi de relaxation dans les variations de la constante élastique des matériaux amorphes.

Abstract. — Ultrasonic attenuation and velocity measurements are reported for the superionic conductor Na $\beta$-alumina for a wide range of temperatures (1.7-80 K) and frequencies (0.5-2.0 GHz). Three acoustic modes were propagated perpendicular to the $c$-axis: longitudinal, transverse polarized perpendicular to the $c$-axis, and transverse polarized parallel to the $c$-axis. In the lower temperature range ($T < 10$ K) the attenuation for all three modes is independent of the ultrasonic frequency and varies as the cube of the temperature. At higher temperatures the attenuation reaches a temperature independent plateau, the height of which depends linearly on frequency. The acoustic phase velocities for the longitudinal mode and the transverse mode polarized perpendicular to the $c$-axis increase logarithmically with temperature at low temperatures, pass through a maximum at approximately 8 K, and then decrease nearly linearly with temperature. The velocity behaviour of the other transverse mode is more complicated.

All the experimental results and particularly the velocity variations, but for one mode, are well-explained in terms of the theory of two-level systems developed for amorphous systems. The logarithmic temperature dependence of the velocity and the $T^3$ temperature dependence of the attenuation are well-known, both theoretically and experimentally, for amorphous insulators. The plateau in the attenuation is not usually observed in amorphous materials. We show that this plateau places restrictions on the distribution function describing the two-level systems and, further, indicates that even for two-level systems of a given energy there is a spectrum of two-level systems-phonon coupling constants.

To describe the attenuation data at temperatures above 10 K, the direct relaxation process of the two-level system does not lead to a sufficiently rapid increase with the temperature. The introduction of a Raman relaxation process

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1. Introduction. — Nonstoichiometric Na $\beta$-alumina belongs to the class of materials known as superionic conductors or solid electrolytes. These materials are interesting because at relatively high temperatures they have a high ionic conductivity due to the fact that one or more types of ions diffuse easily through the lattice. Major interest has been focused on the high temperature properties principally because of potential applications [1]; however, the low-temperature behaviour of such materials has recently drawn attention. The low-temperature ($T \lesssim 3$ K) specific heat of Na, Li, Ag and K $\beta$-alumina presents an excess, compared to the usual Debye value for crystalline insulators, which varies almost linearly with the temperature [2, 3]. In addition, the thermal conductivity of Li, Na and Ag $\beta$-alumina depends on the square of the temperature [4]. More recently the dielectric behaviour of Na $\beta$-alumina has also been studied: the dielectric constant varies logarithmically with temperature while the dielectric absorption depends on the amplitude of the electromagnetic wave [5, 6]. Lastly, the acoustic velocity increases logarithmically with temperature in Na $\beta$-alumina [7]. All these low temperature properties are quite similar to those which have been observed in amorphous materials such as vitreous silica [8, 9].

The low-temperature properties of glasses have been well explained in the framework of the phenomenological theory of two-level systems (T.L.S.) [10, 11]; consequently the same model has been applied to $\beta$-alumina. Although the microscopic nature of these T.L.S. remains unknown, in the case of $\beta$-Al$_2$O$_3$ the anomalous low-temperature properties have been shown to be associated with the alkali cations [2, 3, 4, 6]. $\beta$-alumina consists of spinel-type blocks of aluminum and oxygen separated by planes containing oxygen and the alkali ions. There is normally an excess of the alkali ions over that corresponding to stoichiometry. One possibility for the origin of the T.L.S. is that the excess ions tunnel between interstitial sites in the plane. Another possibility according to which atoms tunnel between off-centre positions has been invoked for sylvanite (Cu$_3$VS$_4$) [12].

In order to gain new information on the amorphous-like behaviour of superionic conductors we have performed acoustic propagation measurements on Na $\beta$-alumina. Our results can be summarized as follows:

— In the lower temperature range ($T < 10$ K) the attenuation is independent of the ultrasonic frequency and varies as the cube of the temperature. This behaviour has previously been observed and explained in amorphous insulators [9, 13, 14].

— At higher temperatures the attenuation becomes independent of the temperature but varies linearly with the ultrasonic frequency. This behaviour has not been seen in standard amorphous materials such as vitreous silica, borosilicate [9] or the amorphous metal PdSiCu [15] although it was predicted many years ago [14]. However, a similar behaviour was observed in the amorphous semiconductor As$_2$S$_3$ [16].

The acoustic phase velocity first increases logarithmically with temperature, as already observed [7], passes through a maximum and then decreases (almost) linearly. Such a linear temperature variation, which seems to be an universal characteristic of amorphous substances [17], is not predicted by theory.

However, as we shall show by a detailed analysis, for quantitative agreement above 10 K it is necessary to take into account a Raman relaxation process in addition to the well-known direct relaxation process. With the inclusion of the Raman relaxation very good agreement is obtained for the attenuation variation at all temperatures and polarizations. Moreover, the introduction of the new Raman relaxation process allows us to explain the velocity variation for the entire temperature range for two of the three polarizations if we add the usual crystalline anharmonicity.

Thus our results indicate that nonstoichiometric Na $\beta$-alumina behaves in some sense as an ideal amorphous material. The results for longitudinal waves have already been reported in a letter [18]. After this introduction, in section 2, we present the experimental method and results, in section 3 we develop the theoretical model; in section 4 we interpret our results, and finally we discuss the results in section 5.

A part of the theory developed here is not entirely new, but it is included in order to present a self-contained article and to introduce some extensions of the standard theory.

However, we are aware of the difficult reading of the manuscript for a non-specialist of amorphous compounds because of the number of different possible approximations. Thus we will give in section 6 an extensive summary of our main results. The non-specialist might prefer to read that section first.
2. Experiments. — 2.1 Experimental method. — Measurements were made on melt-grown crystalline Na β-alumina [19]. The largest dimension of the sample was perpendicular to the c-axis. The 9.6 mm long sample was bonded to a corundum delay rod for the propagation of longitudinal ultrasonic waves perpendicular to the c-axis, and to an AC-cut quartz delay rod for the propagation of transverse waves perpendicular to the c-axis with polarization either perpendicular or parallel to the c-axis. Standard pulse-echo techniques were used to measure the changes of the attenuation and of the velocity over the temperature range 1.5 K-80 K. The sensitivity to attenuation changes was about 0.05 dB cm\(^{-1}\) at a particular frequency, but the absolute accuracy for the comparison of data at different frequencies was only about 0.5 dB cm\(^{-1}\). The sensitivity to phase velocity changes was about 2 \(\times\) 10\(^{-5}\).

2.2 Experimental results. — First we measured the propagation velocity of the three acoustic modes used in our experiments. We obtain 10.4 ± 0.2, 5.65 ± 0.2 and 3.75 ± 0.15 in units of 10\(^5\) cm s\(^{-1}\) for the longitudinal wave, and the transverse waves polarized perpendicular to the c-axis and parallel to the c-axis respectively. From these measurements and using \(\rho = 3.23\) g cm\(^{-3}\) we deduced the values of certain elastic constants: \(C_{11} = 35\), \(C_{12} = 14\) and \(C_{44} = 4.5\) in units of 10\(^{11}\) dyne cm\(^{-2}\). These values are in rough agreement with neutron diffraction measurements [20].

The results for the longitudinal wave attenuation measured at four frequencies ranging from 0.7 to 2 GHz are shown in figure 1, using logarithmic coordinates. The results for the two transverse modes are shown in figures 2 and 3.

Similar features are observed for the three acoustic modes. At the lowest temperatures \((T < 10\) K\)) there is a region where the attenuation for all the frequencies falls on the same line within the experimental accuracy. The slope of this common line is very close to 3, so that the dependence of the attenuation on the frequency and temperature is described in this temperature range by \(\alpha \sim \omega T^3\).

At higher temperatures the attenuation reaches a temperature independent plateau the height of which is frequency dependent. In order to display this frequency dependence the plateau attenuation is plotted as a function of frequency in figure 4. As can be seen, the frequency dependence is linear: the slope of the straight line depends on the acoustic mode. Thus, in this temperature range the attenuation is given by \(\alpha \sim \omega T^0\).
Fig. 3. — Temperature dependent part of the ultrasonic attenuation at three frequencies for transverse waves with propagation direction perpendicular and polarization parallel to the c-axis of a Na β-Al₂O₃ sample. The solid lines are calculated curves with the parameters of table I as discussed in the text.

Fig. 4. — Plateau attenuation extracted from figures 1, 2 and 3 ($\Delta \alpha = \alpha (30 K) - \alpha (2 K)$) versus the ultrasonic frequency in Na β-Al₂O₃. The three symbols are for different acoustic waves propagating perpendicular to the c-axis: o longitudinal, ● transverse polarized along the c-axis, △ transverse polarized perpendicular to the c-axis.

Fig. 5. — Semi-log plot of the relative phase velocity of three acoustic waves propagating perpendicular to the c-axis of a Na β-Al₂O₃ sample. ● transverse wave of frequency 740 MHz polarized along the c-axis, + transverse wave of frequency 740 MHz polarized perpendicular to the c-axis, o longitudinal wave of frequency 1030 MHz. The curves are shifted arbitrarily relative to each other. The zero of the vertical scale is arbitrary.

We have measured the temperature dependence of the ultrasonic velocity at 1.03 GHz for the longitudinal wave and at 0.74 GHz for the two transverse waves. In figure 5 the results at the lowest temperatures ($T < 20 K$) are plotted using semi-logarithmic coordinates. The velocity increases with increasing temperature up to a maximum at about 8 K and then decreases. For the transverse wave polarized along the c-axis the magnitude of the variation is small and the maximum is not seen clearly. However the temperature dependence is in agreement with a logarithmic variation in the range 1.5 K-5 K, at least for the longitudinal wave and the transverse wave polarized perpendicular to the c-axis. In figure 6 the results are plotted using linear coordinates for the entire temperature range. The decrease of the velocity above 10 K is almost linear for the three acoustic modes. This behaviour is observed up to 70 K for the longitudinal wave and at least up to 45 K for the transverse wave polarized perpendicular to the c-axis (at higher temperature the poor signal to noise ratio precludes any measurement). The behaviour of the velocity of the other transverse mode is more complicated. After a roughly linear decrease between 10 and 20 K, the velocity goes through a minimum at about 25 K and increases again. For comparison we have shown also the variation of the longitudinal wave propagating parallel to the c-axis of an α-Al₂O₃ (corundum) sample.
Fig. 6. — Linear plot of the relative phase velocity of three acoustic waves propagating perpendicular to the c-axis of a Na β-Al₂O₃ sample for an extended temperature range. The symbols are as in figure 5. The change of acoustic phase velocity is also shown (triangles) for a longitudinal wave of frequency 1030 MHz propagating along the c-axis of a corundum sample (α-Al₂O₃). The curves are shifted arbitrarily relative to each other. The zero of the vertical scale is arbitrary. The solid lines are total contributions calculated with the parameters of table I.

3. Theory. — 3.1 The Two-Level System Model.

Low temperature dynamical properties of glasses are satisfactorily described by the two-level system (T.L.S.) model proposed by A. H. V. [10] and Phillips [11] which gives the correct temperature dependences for the specific heat, the thermal conductivity, and the acoustic attenuation and velocity [9]. The saturation of the acoustic attenuation is also included among the consequences of the model.

The main feature of the theory is the assumption of the existence in glasses of localized systems with two eigenstates separated by an energy splitting 2E. In addition, it is assumed that the density of states of these systems is very broad (extending from 0 to 0.1 eV) and nearly constant. The predictions resulting from these two simple assumptions are in agreement with many (but not all) experiments on the low temperature behaviour of glasses. Up to this point the nature of the T.L.S. is not specified.

The interpretation of some experiments (especially high temperature acoustic relaxation attenuation) requires a more precise description of the T.L.S. Indeed the real nature of the T.L.S. is not yet firmly established, but they are often thought as particles of mass m (for instance light atoms) which tunnel between two positions corresponding to the minima of a double well potential, separated by a distance l and a barrier height V₀. 2Δ is the potential asymmetry, i.e. the energy difference between the two potential minima. In fact, only two parameters are needed : Δ and

\[ \Delta_0 = \hbar \Omega \left( \frac{\sigma}{\pi} \right)^{1/2} e^{-\sigma} \] (1)

with

\[ \sigma = \left( \frac{2 m V_0 h^2}{\hbar^2} \right)^{1/2} l \] (2)

where \( \Omega \) is the eigenfrequency of the particle in each potential well. The energies of the two eigenstates are

\[ E_{\pm} = \pm \left( \Delta^2 + \Delta_0^2 \right)^{1/2}. \] (3)

Since only two states are considered, a description of the T.L.S. with the help of a fictitious spin \( S = 1/2 \) is possible [21, 9]. The hamiltonian (in diagonal form) of the T.L.S. is then

\[ \mathcal{H} = 2 ES_{z}. \] (4)

Of central importance for this article is the coupling of the T.L.S. with phonons (or elastic strains). An elastic strain \( \varepsilon \) (without indices because we neglect here its tensorial character) modifies the parameters \( \Delta \) and \( \Delta_0 \). We expand \( \Delta \) and \( \Delta_0 \) in series of increasing powers of the strain. For our purpose we can limit ourselves to the second order and we have

\[ \Delta(\varepsilon) = \Delta + \varepsilon \frac{\varepsilon \Delta}{c^2} + \varepsilon^2 \frac{\varepsilon^2 \Delta}{c^4} + \cdots \] (5)

\[ \Delta_0(\varepsilon) = \Delta_0 + \varepsilon \frac{\varepsilon \Delta_0}{c^2} + \varepsilon^2 \frac{\varepsilon^2 \Delta_0}{c^4} + \cdots. \] (6)

From the definition of \( \Delta_0 \) (Eq. (1)) it is easy to see that [11, 21] :

\[ \frac{\varepsilon \Delta_0}{c^2} \simeq \Delta_0 \frac{\varepsilon}{c^2} \approx \Delta_0. \]

\[ \frac{\varepsilon^2 \Delta_0}{c^4} \simeq \Delta_0 \frac{\varepsilon^2}{c^4} \approx \Delta_0. \]

On the other hand, we put

\[ \frac{\varepsilon \Delta}{c^2} = \gamma \] and \[ \frac{\varepsilon^2 \Delta}{c^4} = \delta. \]

Experiments show that \( \gamma \approx 1 \) eV. Moreover, it is usually assumed [22] that \( \delta \approx \gamma \). (This is the same argument which predicts for elastic constants that
In fact, as will be demonstrated in section 4, we have for Na $\beta$-Al$_2$O$_3$, $\delta \gg \gamma$. Then we have $\delta \gg \gamma \gg \Delta_0$. In the basis of the states of the atom in each minimum the Hamiltonian matrix is written
\[ \mathcal{K} = \begin{pmatrix} A(\varepsilon) & -A_0(\varepsilon) \\ -A_0(\varepsilon) & -A(\varepsilon) \end{pmatrix} \] (7)

where $A(\varepsilon)$ and $A_0(\varepsilon)$ are the preceding expansions (equations (5) and (6)). If there is no strain, in the diagonal basis we have
\[ \mathcal{K} = \begin{pmatrix} E & 0 \\ 0 & -E \end{pmatrix} \] (8)

In presence of the strain $\varepsilon$, the Hamiltonian matrix turns out to be:
\[ \mathcal{K} = \begin{pmatrix} E & 0 \\ 0 & -E + \left( \varepsilon^2 + \frac{1}{2} \varepsilon^2 \right)/E \end{pmatrix} \begin{pmatrix} A & -A_0 \\ -A_0 & -A \end{pmatrix} \] (9)

where we have neglected the two derivatives $\partial A_0/\partial \varepsilon$ and $\partial^2 A_0/\partial \varepsilon^2$. Under the operator form we have :
\[ \mathcal{K} = 2E S_x + G_x S_y + G_y S_x + H_x S_x + \delta H_z S_z \] (10)

with
\[ G_x = -2 \gamma \frac{A_0}{E}, \quad G_z = 2 \gamma \frac{A}{E} \]
\[ H_x = -\delta \frac{A_0}{E}, \quad H_z = \delta \frac{A}{E}. \] (11)

The last four equations show that the coupling between the T.L.S. and the elastic strain depends on the parameters $A$ and $A_0$. Even for T.L.S. with a given energy $2E$ there is a distribution of the values of the coupling constants $G_x$, $G_z$, $H_x$ and $H_z$. This distribution is accounted for by the parameter $r = (A_0/E)^2$ where $r_m \leq r \leq 1$. The minimum value $r_m$ corresponds to the smallest value $A_m$ of $A_0$ (see equation (15) below). We can write (omitting the minus sign which does not matter):
\[ G_x = 2 \gamma r^{1/2}, \quad G_z = 2 \gamma (1 - r)^{1/2} \]
\[ H_x = \delta r^{1/2}, \quad H_z = \delta (1 - r)^{1/2}. \] (12)

Finally we write down the coupling Hamiltonian taking into account the tensorial character of the strain and omitting the term which is irrelevant to our calculations:
\[ \mathcal{K}_c = \sum_{s, \beta} (G_{s\beta} S_x e_{s\beta} + G_{s\beta} S_z e_{s\beta}) + \sum_{s, \phi, \psi} H_{s\phi\psi} e_{s\phi} \] (13)
mina experimental results require $\lambda = 0$. In order to simplify the following calculations we now take $\lambda = 0$ and we defer to the Appendix a brief examination of the case $\lambda \neq 0$.

Instead of $d$ and $\omega_0$ two other parameters are more convenient for the forthcoming calculation. They are $E$ and the parameter $r$ defined above. Equation (15) may be replaced by

$$P(E, r) = \left\{ \frac{A}{2} (1 - r)^{\mu - 1/2} r^{-1} \right\}$$

In order to gain a better insight into the physical role of the parameter $\mu$ (when $\lambda = 0$) we have calculated the density of states:

$$n(2E) = \frac{1}{2} n(E) = \frac{N}{\sum_{E_m}^{1} dE} \int_{E_m}^{1} dr P(E, r)$$

where $N$ is the total number of T.L.S. per volume. We compare two distribution functions with different values of $\mu$ but with other common parameters. The results are sketched in figure 7 for $\mu = 0$ and $\mu = 1.5$. The figure shows that an increase of $\mu$ induces a decrease of the density of states for the smallest value of $E$ (and consequently an increase for the largest values because the total number of T.L.S. is assumed to be constant). As a result we may predict some physical consequences. For instance the specific heat, which is proportional to the density of states of low energy, must decrease when $\mu$ decreases.

![Figure 7](image)

3.3 Resonant Acoustic Attenuation and Dispersion. — The saturation of the resonant acoustic attenuation is probably the most striking feature of the low temperature study of glasses and the best proof of the existence of T.L.S. It shows that the acoustic wave interacts with a finite number of excitations. The theory of the effect is well-known [9]. We give below the results for the resonant attenuation and dispersion which are valid when the linewidth may be neglected. In addition, we ignore saturation because we are primarily interested in the influence of the modified distribution function on the results. The inverse mean free path is then

$$l^{-1}(\omega, T) = \frac{\pi}{2} \frac{C}{V_0} \int dE \tanh \beta E \delta \left( E - \frac{\hbar \omega}{2} \right) \times$$

and

$$l^{-1}(\omega, T) = \frac{\pi}{2} \frac{C}{B(1, \mu + 1/2)} \frac{\hbar \omega}{V_0} \tanh \left( \frac{\beta \hbar \omega}{2} \right)$$

where $\omega/2 \pi$ is the elastic wave frequency and $V_0$ is the propagation velocity. $\beta$ has the usual meaning, $\beta = 1/kT$. $B(a, b)$ is the beta function defined as

$$B(a, b) = \int_{0}^{1} dx x^{-1+a}(1 - x)^{-1+b}$$

and

$$C = \frac{N\lambda^2}{2} \frac{\rho V_0^2}{\rho V_0^2} = \frac{\bar{F}}{\rho V_0^2}$$

We take $N\lambda^2/2 = \bar{F}$ because in acoustic experiments we measure only the product $N\lambda$. We also assume $\mu > -1/2$.

Associated with the attenuation there is a velocity change (which may be obtained, for instance, by a Kramers-König transformation) which turns out to be, in the low-frequency range ($\hbar \omega \ll kT$);

$$\frac{\Delta V}{V_0} = \frac{1}{2} CB(1, \mu + 1/2) \ln \left( \frac{T}{T_0} \right)$$

where $T_0$ is some fiducial temperature. This dispersion effect cannot be saturated when the acoustic flux is increased [24].

For comparison with our experimental data the relevant result is: the velocity change due to the resonant effect is logarithmic in temperature and the coefficient of the neperian logarithm is

$$C^* = \frac{1}{2} CB(1, \mu + 1/2)$$

or

$$C^* = \frac{C}{1 + 2 \mu}.$$
3.4 Relaxation through the phonon field. —

Before calculating the relaxational attenuation and dispersion we discuss the different processes by which a T.L.S. population can relax via the phonon field. The coupling hamiltonian (Equation (13)) gives the main relaxation processes for a given T.L.S. \( \varepsilon_{\sigma} \) and \( \varepsilon_{\rho\nu} \) stand for strain components taken at the T.L.S. site. Instead of this form we use the strain associated with each acoustic phonon mode. The hamiltonian becomes:

\[
\mathcal{K}_c = \frac{1}{\sqrt{N}} \sum_{q,\tau} \left( G_{x,\tau} S_x q,\tau + G_{z,\tau} S_z q,\tau \right) + \frac{1}{N} \sum_{q_1, q_2, \tau_1, \tau_2} H_{n,\tau_1,\tau_2} S_x q_1,\tau_1, q_2,\tau_2 \tag{22}
\]

where the sums are over the wavevectors \( q \) and the polarizations \( \tau \). \( N \) is the number of elementary cells in the sample. This form is oversimplified because we have assumed that the coupling constants depend only on the phonon polarization, but not on the wavevector length or direction.

The first term of \( \mathcal{K}_c \) gives the well-known direct (or one-phonon) process [14]. The third term gives a two-phonon process. Because this term can induce a transition between the two-levels by a first order perturbation process it is often called a first order Raman process. The second term acting alone cannot induce a transition between the two-levels, but with the help of the first term it can give a two-phonon process in a second-order Raman process.

The principle of the relaxation rates calculation may be found in many standard textbooks [25]. The main lines are as follows: The strain \( \varepsilon_{q,\tau} \) is written in terms of creation and annihilation operators for the phonon mode \( q, \tau \). The effect of all the modes is taken into account by a sum (simple or double depending on the process) over wavevector and polarization with a restriction in order to conserve the total energy. This sum is easy to do in an isotropic dispersionless medium. Complete elastic isotropy exists in actual amorphous materials, but \( \beta \)-alumina only possesses isotropy around its sixfold axis. However, for the sake of simplicity we assume complete isotropy. Generally textbooks give the results for the Raman processes only in the high temperature regime where the energy splitting \( 2E = \hbar \omega_0 \) of the spin (here the T.L.S.) is very small compared to \( kT \). We give here equations for the three processes valid for any temperature small compared to the Debye temperature (\( \theta_D \) is of the order of 600 K in \( \beta \)-alumina [2]). The only difficulties in the calculation are the evaluation of integrals \( I_3 \) and \( I_1 \) for the second order and first order Raman processes respectively with

\[
I_3(x_0) = \int_{-\infty}^{+\infty} dx \ x(x-x_0)^3 \operatorname{cosech} x \cosh(x-x_0)
\]

and

\[
I_1(x_0) = \int_{-\infty}^{+\infty} dx \ x(x-x_0)^3 \cosh x \operatorname{cosech}(x-x_0).
\]

These two formulas can be written as convolution products. They may be easily calculated by using a double Fourier transform and standard tables [26]. Lastly we have to take into account the distribution of the values of the coupling constants as given by equations (12). Finally our results are as given below.

3.4.1 Direct process (D)

\[
\frac{1}{T_D} = r K_3 T^3 F_3(\beta E) \tag{23}
\]

with

\[
K_3 = \frac{4}{\pi^2} \sum_{\tau} \frac{\gamma_{T_1}^2}{\tau \rho \nu_{\tau}^2} \tag{23a}
\]

and

\[
F_3(u) = u^3 \coth u \tag{23b}
\]

3.4.2 First order Raman process (R 1)

\[
\frac{1}{T_1} = r K_5 T^5 F_5(\beta E) \tag{24}
\]

with

\[
K_5 = \frac{1}{2} \sum_{\tau} \left( \frac{\delta_{\tau,\sigma}}{(\rho \nu_{\tau}^2)} \right) \tag{24a}
\]

and

\[
F_5(u) = \frac{u}{70} (u^2 + \pi^2) \times \left( u^4 - \pi^2 u^2 + \frac{10}{3} \pi^4 \right) \coth u \tag{24b}
\]

3.4.3 Second order Raman process (R 2)

\[
\frac{1}{T_2} = 4 (1 - r) K_5 T^5 F_5(\beta E) \tag{25}
\]

with

\[
K_5 = \frac{1}{8} \rho \frac{\gamma_{T_1}^2}{\nu_{\tau}^2} \tag{25a}
\]

and

\[
F_5(u) = \frac{u}{30} (u^2 + \pi^2) (3 u^2 + 2 \pi^2) \coth u \tag{25b}
\]

The minimum relaxation times, noted \( T_1^\infty \), are obtained if: i) \( r = 1 \) for the direct and the first order Raman processes; ii) \( r = 1/2 \) for the second order Raman process. When all three processes are active the relaxation \( T_1 \) is given by

\[
\frac{1}{T_1} = \frac{1}{T_D^\infty} + \frac{1}{T_1^{R1}} + \frac{1}{T_1^{R2}}. \tag{26}
\]

We show in the discussion of our results that the direct process is dominant at low temperatures, the first order Raman process is dominant at high
temperature and the second order Raman process is always negligible. This result can be seen in figure 8 where we have plotted the values of $1/T_1$ versus the T.L.S. energy for two temperatures with the numerical values obtained in our experiments for the three coefficients $K_3$, $K_5$, and $K_7$ (note that $K_3$ is related to $K_3$). It is clear that at 1 K the direct process is dominant in the relaxation while at 20 K the first order Raman process is the more efficient process.

As a result of the modulation of the splitting $2E$ the T.L.S. population is periodically driven out of equilibrium. The relaxation towards equilibrium occurs with a characteristic time $T_1$ which is the longitudinal (or population) relaxation time. Because of this delay (or hysteresis) there is an energy dissipation and the elastic wave is slowed.

The theory of this effect may be found in many places [14, 9]. We only give the results. The attenuation and dispersion of an elastic wave are both described by the complex change of the elastic constant $\delta c(\omega, T)$:

$$\frac{\delta c}{c_0} = -\frac{N}{c_0} \int d(\beta E) \operatorname{sech}^2 \beta E \times$$

$$\times \int_{r_m}^1 \frac{G_s^2 P(E, r)}{1 + i\omega T_1(E, r, T)} \quad (28)$$

where $c_0$ is the elastic constant without coupling between the wave and the T.L.S. For the dominant relaxation processes we have

$$\frac{1}{T_1(r, E, T)} = \frac{r}{T_1^m(E, T)} .$$

If we put $v = \omega T_1^m$ we obtain with the help of eqs. (16) and (12):

$$\frac{\delta c}{c_0} = -\frac{P_T}{c_0} \int d(\beta E) \operatorname{sech}^2 \beta E \int_{r_m}^1 dr \frac{(1 - r)^{\mu + 1/2}}{r + iv} .$$

(29)

It is worthwhile to notice that the distribution of the relaxation times for a T.L.S. population with a given splitting energy $2E$ is rigorously taken into account when the inner integral is calculated.

Equation (29) does not seem to have an analytical solution, but we can look at the asymptotic behaviours for $v \gg 1$ (low temperature regime) and for $v \ll 1$ (high temperature regime). Elsewhere, we have to use a computer. In order to discuss the limiting behaviours we first put

$$I(v, \mu) = \int_{r_m}^1 dr \frac{(1 - r)^{\mu + 1/2}}{r + iv} .$$

(30)

In the limit $v \gg 1$ it is easy to show that :

$$I(v, \mu) \simeq -\frac{i}{v} B(1, 3/2 + \mu) + \frac{1}{v^2} B(2, 3/2 + \mu) .$$

(31)

The other limit ($v \ll 1$) is more complicated. It can be shown (see Appendix) that the result is :

$$I(v, \mu) \simeq -\ln v - \frac{\pi}{2} + \text{real constant} .$$

(32)
An important point to notice is that in this last regime the results do not depend on the value of the parameter \( \mu \), except through a real additive constant.

Another point deserves some discussion. The quantity \( v \) depends on the energy \( E \) which is the variable for the outer integral (Eq. (29)). For all the processes which take a part in the relaxation of the T.L.S., the relaxation time \( T_1 \) is a decreasing function of \( E \). Therefore we can imagine the case where \( v \gg 1 \) for small \( E \) and \( v \ll 1 \) for large \( E \), and the regime seems to be undefined. Fortunately, in the outer integral there is a function \( \text{sech}^2 (\beta E) \) which exponentially decreases when \( E \approx kT \). It serves as a cut-off function for the T.L.S. with energies larger than a few times \( kT \). Therefore, in defining our regimes (\( v \gg 1 \) or \( v \ll 1 \)), we only need to consider T.L.S. with energies up to \( kT \) and then it appears that the two regimes are generally well defined.

Figure 8 gives the variation of \( \omega/(\pi E, T) = 1/T_1^0 \) versus \( E \) at two temperatures for the three relaxation processes at frequency \( \omega/2 \pi = 1 \) GHz which lies in our experimental range. The figure shows that the distinction between the regimes \( v \gg 1 \) and \( v \ll 1 \) has a very clear meaning for the R 1 and R 2 processes. In fact, for these processes all the T.L.S. may be simultaneously in the case \( v \ll 1 \) which is then rigorously defined. For the direct process there might be some difficulties because all the T.L.S. do not cross the condition \( v \approx 1 \) together. Therefore the intermediate region between the regime \( v \gg 1 \) and the regime \( v \ll 1 \) spreads over a broad temperature range. Fortunately, in our experimental conditions (relatively high frequencies) the condition \( v \approx 1 \) is obtained when the R 1 process becomes dominant. Therefore the two regimes are well defined in our case.

With \( f(v, \mu) \) known the outer integral of equation (29) remains to be done. Using the explicit dependence of \( T_1^0 \) on \( E \) and \( T \) we can continue the calculation of the relaxational effects.

We consider now the different regimes.

3.5.1 Low temperature regime. — In this case the dominant relaxation process is the direct one. From equations (29), (30), (31), (23) it follows that

\[
\frac{\delta c}{c_0} = - \frac{\pi^6}{42} CB(2, 3/2 + \mu) \frac{K_3^2}{\omega^2} T^6 \times \\
\int_{\beta E_m}^{\beta E_m} du \, u^6 \text{cosech}^2 u
\]

or

\[
\text{Re} \left( \frac{\delta c}{c_0} \right) \simeq - \frac{\pi^6}{42} CB(2, 3/2 + \mu) \frac{K_3^2}{\omega^2} T^6 (33b)
\]

because we can extend the integration limits to 0 and \( \infty \):

\[
\text{Im} \left( \frac{\delta c}{c_0} \right) = CB(1, 3/2 + \mu) \frac{K_3}{\omega} T^3 \left[ \frac{1}{8} \times \\
\int_{2\beta E_m}^{2\beta E_m} du \, u^3 \text{cosech} u \right] (34a)
\]

or

\[
\text{Im} \left( \frac{\delta c}{c_0} \right) \approx \frac{\pi^4}{64} CB(1, 3/2 + \mu) \frac{K_3}{\omega} T^3. (34b)
\]

The acoustic dispersion and attenuation are respectively related to the real and imaginary parts of the complex elastic constant by

\[
\frac{\delta V}{V_0} = \frac{1}{2} \text{Re} \left( \frac{\delta c}{c_0} \right) \quad \text{and} \quad l^{-1} = \frac{\omega}{V_0} \text{Im} \left( \frac{\delta c}{c_0} \right).
\]

Finally we have

\[
\frac{\delta V}{V_0} = - \frac{\pi^6}{84} CB(2, 3/2 + \mu) \frac{K_3^2}{\omega^2} T^6 (35)
\]

and

\[
x = l^{-1} = \frac{\pi^4}{64} CB(1, 3/2 + \mu) \frac{K_3}{V_0} T^3. (36)
\]

In this regime the inverse mean free path is independent of the frequency and is proportional to the cube of the temperature. The velocity varies as \( T^6 \omega^{-2} \).

3.5.2 High temperature regime. — In this regime, \( v \) is much less than 1 and the dominant relaxation process in this temperature range is the first order Raman process. With our choice of \( \hat{z} = 0 \), we obtain from equations (29), (30), (32), (24):

\[
l^{-1} = \frac{\pi}{2} \frac{C \omega}{V_0} \quad \text{(37)}
\]

In this case the attenuation is temperature independent (a plateau is expected) and it varies linearly with the frequency. This behaviour has already been predicted by Jäckle [14]. Concerning the velocity we find:

\[
\text{Re} \left( \frac{\delta c}{c_0} \right) = C \int_0^\infty du \, \text{sech}^2 u \left[ \ln \omega - \ln K_7 - 7 \ln T - \ln F_7(u) \right] (38a)
\]

\[
= C \left[ \ln \omega - \ln K_7 - 7 \ln T - \int_0^\infty du \, \text{sech}^2 u \ln F_7(u) \right]. (38b)
\]
Omitting terms which are pure numbers, we have
\[ \frac{\delta V}{V_0} = \frac{C}{2} \ln \omega - \frac{7}{2} \ln T. \] (39)

The frequency and temperature dependences are both logarithmic. We have already mentioned in what sense these results are independent of the parameter \( \mu \). But more important is the following remark: even though we are considering an effect due to the population relaxation our results are independent of the \( T_1 \) value. More precisely the attenuation is completely independent of the relaxation process (provided it produces the condition \( v \ll 1 \)) and the relaxation appears in the velocity change only by the number \( 7 \) as a factor of \( \log T \) (due to the \( T^7 \) dependence of \( R \)) and in additive constants (not written). Moreover, in spite of the condition \( v = \omega T_1^* \ll 1 \) which looks like a hydrodynamic regime condition, we do not have an \( \omega^2 T_1^* \) law for the attenuation. The reason for that is explained in the Appendix.

4. Interpretation. — 4.1 LIMITING BEHAVIOURS. —
In the theoretical part we showed that certain limiting behaviours are characteristic of the amorphous compounds.

— In the low temperature limit the relaxation part of the velocity change is much lower than the resonant part. Thus only the latter has to be considered. According to equation (20) the velocity must change as the logarithm of the temperature. From figure 5 it is clear that the velocity depends logarithmically on temperature below 5 K for two polarizations. This behaviour has already been reported by us for longitudinal waves [7]. From the slope we can deduce the value of \( C' \) for the various modes. The results are quoted in table I. In the same conditions, the attenuation must show an increase when the temperature decreases for very low level of acoustic power. We have not yet been able to observe this increase because of the small magnitude of the effect in our temperature range.

— The second limiting regime is the high temperature domain \((T > 20 \, K)\). As noted in the theoretical section Jäckle pointed out [14] that this part of the attenuation must be temperature independent and must change linearly with the frequency. This behaviour, of course, borne out by the experiment for the three polarizations studied as the inspection of figures 1, 2 and 3 shows. Again we note that we already reported this behaviour for longitudinal waves [18] in \( \beta-Al_2O_3 \). This experiment recalled an old prediction of T.L.S. theory and confirmed its relevance to the description of amorphous behaviour. Equation (37) shows that the limiting value of the plateau for the attenuation is a measurement of the coupling constant \( C \). Table I gives the value of this constant for each of the three polarizations studied. We note that if we use the Phillips distribution the value of \( C' \) and \( C \) should be the same. We will return to this point later. We have already emphasized that the results for the attenuation are independent of the relaxation process. This is not true for the velocity. Thus we postpone the discussion of the velocity in this regime until after the identification of the dominant relaxation process in this temperature range.

4.2 INTERMEDIATE REGIME. — For this identification we come back to intermediate temperature range where \( v = \omega T_1^* \ll 1 \). No approximation is possible and no algebraic expression is known for the attenuation. Thus we made a numerical calculation of equation (29) using equations (23-26) for \( T_1^* \). In this calculation \( K_3 \) and \( K_7 \) were adjusted in order to get the best fit possible. The value of \( C \) was deduced from the experimental plateau as explained earlier. At this point it is necessary to return to the difference we measured between \( C \) and \( C' \) since we used this difference to fix \( \mu \). As noted above, the very simple distribution proposed by Phillips leads to an equality between the value of \( C \) and \( C' \) (\( C \) fixes the value of the attenuation plateau according to Eq. (37) and \( C' \) the slope of the low-temperature logarithmic velocity variation according to Eq. (20)). This equality is not borne out by the experiments. The existence of a plateau for the attenuation implies necessarily that \( \lambda = 0 \) (see Appendix). This is the reason why we put \( \lambda = 0 \) in equation (15). The value of \( \mu \) is then fixed by the ratio of \( C \) to \( C' \) (see equation (21)). From the experiment with longitudinal waves we find
\[ \mu = 0.45 \pm 0.15. \]
From the data with transverse waves we find
\[ \mu = 1.4 \pm 0.5. \]
It is surprising to obtain such a difference between the values of \( \mu \) for two different polarizations of the

Table I. — Summary of the parameters used to describe the propagation of acoustic waves perpendicular to the c-axis of a nonstoichiometric Na \( \beta \)-alumina sample. All these parameters are either directly measured in this work, or deduced from a numerical fit. Their meanings are given in the text.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Longitudinal</th>
<th>Transverse ( u \perp c )</th>
<th>Transverse ( u \parallel c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V ) ((10^5 , \text{cm s}^{-1}))</td>
<td>10.4</td>
<td>5.65</td>
<td>3.75</td>
</tr>
<tr>
<td>( C' )</td>
<td>( 3.6 \times 10^{-5} )</td>
<td>( 3.1 \times 10^{-5} )</td>
<td>( \leq 5 \times 10^{-6} )</td>
</tr>
<tr>
<td>( C )</td>
<td>( 7.1 \times 10^{-5} )</td>
<td>( 14.5 \times 10^{-5} )</td>
<td>( 3 \times 10^{-5} )</td>
</tr>
<tr>
<td>( \gamma ) ((\text{eV}))</td>
<td>0.21</td>
<td>0.17</td>
<td>0.05</td>
</tr>
<tr>
<td>( \mu )</td>
<td>0.4</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>( K_3 ) ((\text{c.g.s.}))</td>
<td>3.6 \times 10^{6}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( K_4 ) ((\text{c.g.s.}))</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( K_5 ) ((\text{c.g.s.}))</td>
<td>( 15 (\delta \sim 100 , \text{eV}) )</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( D ) ((\text{K}^{-4}))</td>
<td>( 10^{-11} )</td>
<td>( 4 \times 10^{-11} )</td>
<td>-</td>
</tr>
</tbody>
</table>
acoustic wave. We have no satisfactory explanation for that. One possibility is that the two elastic waves are not coupled to exactly the same types of T.L.S. Now we are left with only two parameters \(K_3\) and \(K_7\) and these parameters are the same for all polarizations.

In an attempt to keep the physics as simple as possible we considered at first only the direct mechanism in calculating the attenuation. That is we set \(K_7\) to zero. Figure 9 shows the calculated curve that we found for two values of \(K_3\) at \(\omega/2\pi = 1950\) MHz. Shown too are the experimental points to facilitate the comparison of theory and experiment. The smallest value of \(K_3\) leads to a correct fit for the lowest temperature range where the \(T^3\) law is true. But at high temperature the results are very bad. On the contrary, the highest value of \(K_3\) leads to a rough accord at high temperatures but not at low temperatures. More, for the last value of \(K_3\), the calculated curve cuts the experimental one showing that it is hopeless to try to realize a fit with the direct process only.

Fig. 9. — Plot of the calculated relaxation part of the attenuation (normalized to the plateau value) of a longitudinal acoustic wave propagating perpendicular to the \(c\)-axis of a \(Na\beta\text{-Al}_2\text{O}_3\) sample. The parameters are those of table I, at a frequency of \(1\,990\) MHz, but without the Raman processes \((K_5 = K_7 = 0)\). The two curves are for two different values of the coefficient \(K_3\) \((K_3 = 3.6 \times 10^6\) c.g.s. and \(50\,K_3)\). Also shown are the experimental data of figure 1 at the same frequency.

Thus we add the Raman processes. It has been noted in the theoretical part that the coefficients for the direct process and the second order Raman are related. It will be seen below that we must adopt for \(K_3\) the lowest value of figure 9, i.e. \(K_3 = 3.6 \times 10^6\) c.g.s.

With this value we can calculate the constant \(K_5\) which governs the \(R\) 2 process; we find \(K_5 = 0.25\) c.g.s. With these two values we compute the corresponding relaxation rates (see Fig. 8). The \(R\) 2 process is negligible as compared to the direct process at least up to \(20\) K for the relevant T.L.S. The addition of the first order Raman process to the direct process gives the calculated curves in figures 1, 2 and 3 for the different polarizations and at the different experimental frequencies, using the same values of \(K_3\) and \(K_7\) for these three figures. The values of \(C\) are obviously different for the three waves. (They are given in table I.) The values of \(\mu\) were chosen as 0.4 for the longitudinal wave and 1.4 for the two transverse waves. An inspection shows that the results are very good indeed for the transverse wave polarized in the plane (motion perpendicular to the \(c\)-axis). The fit is less good for the longitudinal mode and the second transverse mode (motion parallel to the \(c\)-axis). A slight decrease of the \(K_7\) value would improve the fit for the longitudinal wave and a slight increase would improve the fit for the transverse wave polarized along the \(c\)-axis. The values of \(K_3\) and \(K_7\) are quoted in table I. However the value that we deduce for \(\delta\) \((\delta \sim 100\) eV\) from \(K_7\) is about three orders of magnitude larger than we can expect by comparison with what is generally true for crystals \((\delta \sim \gamma)\) [22]. But such a large coefficient has already been suggested for amorphous \(As_2Se_3\) and \(As_2S_3\) to explain the shape of the thermal conductivity curve [27]. Hence it appears that \(\delta\) is very large in amorphous compounds. From the \(K_3\) value we can deduce the value of \(\sum \frac{\gamma^2}{\tau\rho v_s^2}\). We find \(1.0 \times 10^{-34}\) c.g.s.

On the other hand, using the values of \(C\) for the three polarizations and taking \(P = 2 \times 20^{33}\) erg\(^{-1}\) cm\(^{-3}\) from the specific heat measurements [3], we find \(\sum \frac{\gamma^2}{\tau\rho v_s^2} \simeq 0.7 \times 10^{-34}\) c.g.s. These two results are in remarkably good agreement with each other in view of the fact that we have supposed \(\beta\text{-Al}_2\text{O}_3\) to be an isotropic material.

Finally we note that it is only fortuitous that the \(T^3\) law for the measured attenuation extends over so wide a range in temperature since it holds theoretically only when the direct process is dominant. The experimentally observed behaviour results from a competition between the rapid increase due to the \(R\) 1 process and the bending over when the regime change \((\omega T_1^m \simeq 1)\) occurs.

4.3 VELOCITY. — We return to the discussion of the velocity. At low temperatures the experimental curves show logarithmic variations (see Fig. 5). At higher temperatures they bend over and decrease almost linearly with the temperature. This linear decrease has already been observed in several amorphous compounds [17] and it has been proposed [28]
that this experimental fact might be explained by
a special choice of the density of states of T.L.S.
We propose here another explanation based on the
fact that the first order Raman process becomes
dominant around 10 K.

We attribute the total velocity variation to three
effects: resonance, relaxation, and anharmonicity.
We first discuss the results for longitudinal waves.
The resonance contribution is given simply by
equation (20). Using $\mu = 0.4$ we compute the curve labelled resonance in figure 10. The value of $\mu$ is the
same as that used to fit the attenuation data.

The first order Raman process enters in two important
ways. First, it is responsible for the transition to the
$v \ll 1$ regime at $T \sim 10$ K. Second, the temperature
variation in this regime is $- (7/2) C \ln T$ where the
factor 7 comes from the temperature dependence of
the first order Raman process.

Finally, as in any material, there must be some
anharmonic phonon interactions which induce tem-
perature dependent variations in the velocity and
length. The temperature dependence is of the form [29]
$- D_1 T^2$ at low temperatures. Taking $D_1 = 10^{-11}$ K$^{-4}$
for longitudinal waves we compute the curve labelled
anharmonicity in figure 10. The order of magnitude
of $D_1$ is compatible with that found for other mate-
rials (29) and is not too different from that found
for pure corundum ($\alpha$-Al$_2$O$_3$). We measure

$$ D_1 = 2.5 \times 10^{-12} \text{ K}^{-4} $$

for longitudinal waves propagating along the $c$-axis
in pure corundum.

The sum of the three contributions gives the curve labelled total in figure 10. Considering the extended
temperature range covered, the agreement between the
calculated and measured curves is excellent. It is striking that the resultant temperature depend-
ence is almost linear over a wide range. More striking
is the fact that the small departures of the data from
linearity are reproduced quite closely by the cal-
culated curve.

Using the same curve fitting procedure (with
$\mu = 1.4$ and $D_1 = 4 \times 10^{-11}$ K$^{-4}$) we obtain
excellent agreement between theory and experiment
for the transverse mode polarized perpendicular
to the $c$-axis. The results are shown in figure 6.

Figure 6 also shows our attempts to fit the velocity
data for the transverse mode polarized parallel to the
$c$-axis. We have not been able to fit these data, even
for the roughly linear range of 10-20 K. Apparently
other processes are involved for this mode.

5. Discussion. — We now compare our results
with other data on $\beta$-Al$_2$O$_3$, namely low-temperature
dielectric measurements and thermal conductivity
experiments. In addition, we discuss the applicability
of our conclusions to true amorphous materials.

It is well-known from the study of amorphous
insulators that ultrasonic and dielectric experiments
yield similar information [30]. Thus we compare our
findings with the results of low-temperature micro-
wave dielectric measurements in Na $\beta$-aluma. At
the lower temperatures the results from the two types
of experiments are in qualitative agreement. The
logarithmic increase of the ultrasonic velocity below
about 5 K corresponds to the logarithmic decrease
of the dielectric constant over the same temperature
range. Strom, et al. [5] mention that their dielectric
absorption results (at 10 GHz) are consistent with
a $T^3$ temperature dependence between 5 and 20 K.
Our ultrasonic absorption measurements (0.5-2 GHz) give the same temperature dependence in the 5-15 K range. At higher temperatures there are marked differences between the ultrasonic and dielectric absorption data. Whereas the ultrasonic attenuation exhibits a plateau as a function of temperature above approximately 20 K, the dielectric absorption shows a shoulder at 20 K but no plateau. The shoulder is probably due to the regime change ($\omega T_D^m$ ~ 1). The dielectric absorption at higher temperatures has been attributed to another mechanism [31] which does not seem to be observable with an ultrasonic wave.

The linear decrease of the ultrasonic velocity above the maximum appears to be a common feature of all amorphous materials, both insulators and metals [17], but a corresponding increase of the dielectric constant has never been reported. As explained above, the approximately linear decrease of the velocity in Na $\beta$-Al$_2$O$_3$ is due to a rather fortuitous combination of logarithmic terms (due to the T.L.S.) and a $T^4$ term (due to anharmonicity). Although thermal expansion may have an effect on the dielectric constant, there is no effect corresponding to the anharmonic phonon interactions which contribute to the velocity decrease. Thus, the temperature dependencies of the two phenomena may be different in this temperature range.

Just as the ultrasonic velocity shows a maximum as a function of temperature, the dielectric constant shows a minimum. Such minima have been observed in Na $\beta$-Al$_2$O$_3$ by Anthony and Anderson [6] at frequencies from $10^5$-$10^6$ Hz and by Strom, et al. at 10 GHz. The temperature of the minima varies with frequency approximately as $\omega^{1/3}$ for the data of Anthony and Anderson. This is the frequency dependence expected if the minimum is due to a competition between the resonant part and the relaxational part in the regime $\omega T_D > 1$ with $T_D$ due to the direct process. Actually, at higher temperatures the Raman process becomes dominant leading to a weaker frequency dependence of the minima. A weaker dependence is implied by the 10 GHz data of Strom, et al. where the minimum is observed at ~ 8 K while an $\omega^{1/3}$ extrapolation of Anthony and Anderson’s results predicts a minimum at ~ 40 K.

We now turn to thermal conductivity measurements in $\beta$-Al$_2$O$_3$. We have already mentioned that Leadbetter, et al. [27] have invoked a phonon attenuation process originating from the coupling term in the hamiltonian which is quadratic in phonon operators in order to explain the maximum-minimum observed for the thermal conductivity of some amorphous materials. This term is also responsible for the R1 relaxation process. Anthony and Anderson have measured the thermal conductivity of $\beta$-Al$_2$O$_3$ samples doped with different alkaline ions [4]. For Ag and Na doped samples they observed a maximum-minimum too. They were able to interpret their data by introducing an ad-hoc hypothesis. They assumed the phonon mean free path has an abrupt drop at a frequency $\omega_0$, which is one of their free parameters; in fact either a rapid decrease (with a $T$ dependence stronger than 3), or a discontinuity can explain the experimental curves. We suggest (as Leadbetter, et al. have done) that the Raman attenuation process is strong enough to give a rapid decrease of the phonon mean free path in the relevant temperature range. This mechanism provides a physical basis for Anthony and Anderson’s assumption. If the temperature is low compared to Debye temperature ($T_D \approx 600$ K) the phonon Raman attenuation can be exactly calculated. For a phonon mode with polarization $\tau$ we find:

$$l_{\alpha,\tau}^{-1} = \frac{n_0 k^5 T^3}{\pi \hbar \nu \rho v_\tau^3} \sum_a \frac{H_{X,\tau a}^2}{\rho v_a^5} x \left(\frac{x^2 + \pi^2}{4}\right)$$

(40)

with $x = 1 - \frac{1}{2} \beta \omega_0$.

Equation (40) is valid for any frequency or temperature (provided $T \ll T_D$). Taking into account our result for coefficient $K_1$ we can deduce a mean value for the coupling coefficients $H_{x,ta}$. Therefore without introducing free parameters (the only problem is with the mean value calculation) we find a maximum for the thermal conductivity located around 10 K in agreement with experiment on Na $\beta$-Al$_2$O$_3$. In our opinion this is a confirmation of the strength of the non-linear coefficients $H_{x,ta}$.

From our values of $C$ we can deduce corresponding values of the coupling constant $\gamma$. We find $\gamma = 0.21$ eV, 0.17 eV and 0.05 eV for the longitudinal wave, the transverse wave polarized perpendicular to the c-axis, the transverse wave polarized parallel to the c-axis respectively. These values compare well with the values $\gamma = 0.3$ eV and $\gamma = 0.2$ eV of Anthony and Anderson [6], which are actually mean values deduced from the relaxation part of the dielectric constant and from the thermal conductivity respectively.

Finally we would emphasize that our distribution function has some advantages over the function used by Anthony and Anderson [6, 28]. In particular our numerical results are independent of the cut-off value of the energy and of the minimum value $r_m$ of the quantity $r$. In addition the distribution function of Anthony and Anderson is incompatible with the observation of a plateau in the ultrasonic attenuation.

We now wish to compare our results with ultrasonic measurements on standard amorphous materials. Two special features of our data are the plateau in the attenuation and the evidence for a Raman process at temperatures above about 10 K. These features have not been observed in well-studied amorphous materials, apparently because the attenuation above 5 K is dominated by thermally activated transitions [9].
Results somewhat similar to ours have been observed in the amorphous semiconductor As₂S₃. The ultrasonic attenuation in the frequency range 10-500 MHz was studied by Ng and Sladek [16] from 1.5 K to 480 K. Their experiments show clearly, in the temperature range around 100 K, an attenuation which varies linearly with frequency and is almost independent of temperature. At the lowest temperatures the attenuation decreased abruptly but did not attain a T¹ law. They fitted their data with the relaxation contribution as calculated by Jäckle [14] (equation (29) above) with a particular distribution function which is the product of a centred gaussian function by a displaced gaussian function. Although the expression of the attenuation (equation (37)) in the limit regime (ωT₀ ≪ 1) was not given, the plateau is necessarily included in the integral equation and in the numerical calculation. But the analysis in terms of the relaxation of the T.L.S. is restricted to the attenuation and it is difficult to evaluate the consequences of their particular choice of the distribution function. In a more recent work Claytor and Sladek [32] analyse their velocity measurements in As₂S₃ and As₂Se₃ with a somewhat different procedure.

A difficulty arises when we compare the analysis of Ng and Sladek and the interpretation of the thermal conductivity of As₂S₃ by Leadbetter, et al. [27]. Ng and Sladek did not take into account the Raman process as we did for Na β-Al₂O₃ in this paper and they obtained a very good fit. On the contrary, Leadbetter, et al. suggested that the maximum-minimum in the thermal conductivity of the same compound is a consequence of a Raman process with a very large coupling constant.

In metals the problem is more complicated because of the strong coupling of the T.L.S. with the conduction electrons. At the present time the analysis of the experimental results is restricted to the low temperature range below about 10 K [23]. However, the velocity variation is similar in all the amorphous materials investigated up to this time [17]. It would be interesting to try to fit the linear decrease of the sound velocity in insulators or in metals with contributions analogous to those which have been shown to work well in Na β-Al₂O₃.

It is worthwhile to apply the ideas developed in the present article to other experimental results on amorphous materials. One of our predictions (Equation (39)) is that the relaxation contribution to the velocity in the regime v ≪ 1 is:

\[
\frac{\Delta v}{v} = \frac{C_{us}}{2} \ln \omega - n \frac{C_{us}}{2} \ln T
\]

(41)

where n = 3 or 7 depending on the dominant relaxation process (D or R). A similar prediction evidently holds for the dielectric constant change (with a different definition of the coefficient C):

\[
\frac{\Delta \varepsilon}{\varepsilon} = - C_{em} \ln \omega + nC_{em} \ln T
\]

As an example, dielectric constant measurements on the true amorphous material BK 7 [28] show that the different regimes are experimentally well defined (see Fig. 3 of Ref. [28]). For temperatures higher than the minimum the ln(T/ω) dependence is clearly evident which implies λ = 0. Since the experiments were performed under conditions such that v ≪ 1 when the direct relaxation process is dominant, the coefficient n in equation (42) must be equal to 3. We compare the slopes in the resonant and relaxation cases. The slope of the relaxation contribution is just 3 C_em. The coefficient of the logarithmic resonant contribution is 2 C_em with

\[2C_{em} = 2 C_{em}/(1 + 2 \mu)\]

by analogy with equation (20). We can deduce μ by taking the slopes from figure 3 of reference [28]. We have

\[
\frac{3 C_{em} - 2 C_{em}}{2 C_{em}} = \frac{1 + 6 \mu}{2} \approx \frac{1}{2}
\]

which leads to μ ≈ 0. The original distribution function of Phillips [11] (λ = 0, μ = 0) is found to describe the results for BK 7.

The ultrasonic velocity measurements of Bellessa [17] are also explained in terms of the present ideas. Bellessa found a logarithmic frequency dependence for the velocity for temperatures higher than the maximum as well as the usual logarithmic temperature dependence below the maximum in both an insulating glass and a metallic glass. More precisely, the numerical coefficients for the two logarithmic dependencies are of the same order of magnitude. Comparing equations (20) and (39) we see that such behaviour is expected. The T.L.S. theory is therefore able to explain qualitatively and quantitatively most of the experimental results obtained on amorphous materials.

6. Summary of main results. — Table II summarizes the main results we obtain for the attenuation and phase velocity variations due to the coupling between an ultrasonic wave and a double distribution of two level systems (T.L.S.). Double distribution means that there is not only a distribution of the energy splitting between the two levels for different T.L.S. but there is also a distribution of the coupling between T.L.S. of a given energy and the wave. A star in the table indicates an effect we have actually observed.

We separated, as usual, our results into a resonant part and a relaxation part. Resonant part means the contribution to the attenuation due to the resonant interaction between the wave and those T.L.S. having an energy splitting corresponding to the
Table II. — Summary of the theoretical results established in the article. A full description of this table is given in section 6. The stars mean that the effect has been observed in these experiments.

<table>
<thead>
<tr>
<th>Attenuation</th>
<th>Relative phase velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resonant relaxation</td>
<td></td>
</tr>
<tr>
<td>$B \left(1, \frac{1}{2} + \mu \right) C \omega \tanh \frac{\hbar \omega}{2kT} \frac{1}{(1 + \Phi/\Phi_0)^{1/2}}$</td>
<td>$B \left(1, \frac{1}{2} + \mu \right) C \ln T$ *</td>
</tr>
<tr>
<td>— direct process</td>
<td></td>
</tr>
<tr>
<td>$\omega T_1^m \gg 1$</td>
<td>$B \left(1, \frac{3}{2} + \mu \right) C K_3 T^3$ *</td>
</tr>
<tr>
<td>$\omega T_1^m \ll 1$</td>
<td>$C \omega$</td>
</tr>
<tr>
<td>— first order Raman process</td>
<td>$\omega T_1^m \gg 1$</td>
</tr>
<tr>
<td>$\omega T_1^m \ll 1$</td>
<td>$B \left(1, \frac{3}{2} + \mu \right) C K_7 T^7$</td>
</tr>
<tr>
<td></td>
<td>$B \left(1, \frac{3}{2} + \mu \right) C K_3 T^{14} \omega^{-2}$</td>
</tr>
</tbody>
</table>

frequency of the wave. The relaxation part means the contribution to the attenuation due to the perturbation by the wave of the energy splitting of the T.L.S. All the T.L.S. participate in that part.

The resonant results are well known. The attenuation changes with the temperature as the population difference of the two energy levels. The factor $(1 + \Phi/\Phi_0)^{-1/2}$ describes the saturation effect: the resonant attenuation may go to zero if the acoustical flux $\Phi$ is stronger than a critical flux $\Phi_0$. The velocity changes as the logarithm of the temperature. The function $B(1, 1/2 + \mu)$ is the Beta-function and it is needed because of the particular distribution function chosen in this article (see § 3.2).

The relaxation results are more novel because we take into account not only the direct relaxation process of the T.L.S. but we add the first order Raman process (see the Hamiltonian equation (22) and the comments below). Since there is a distribution of the coupling constant and of the energy of the T.L.S., the relaxation time $T_1$ is a function of three variables: $E$, half the energy; $T$, the temperature; and $r$, the parameter describing the coupling distribution for the T.L.S. of a given energy (see equation (12) for the definition of $r$). We show, however, that for the two dominant relaxation processes $T_1$ can be written as

$$T_1(E, T, r) = T_1^m(E, T)/r \quad \text{with} \quad r_m < r < 1$$

$T_1^m$ appears as the minimum relaxation time for the T.L.S. of a given energy. There exists two limiting regimes, one is for $\omega T_1^m \ll 1$ whatever is the energy separation and the other for $\omega T_1^m \gg 1$. By chance, in our experiments the regime change $(\omega T_1^m \approx 1)$ occurs at about the same temperature as the emergence of the Raman process. We are therefore in the simple alternative: $\omega T_1^m \gg 1$ with $T_1^m$ due to the direct process or $\omega T_1^m \ll 1$ with $T_1^m$ governed by the Raman process.

One of the most interesting result of table II is the attenuation law when the condition $\omega T_1^m \ll 1$ holds. It is clear that whatever is the dominant relaxation the attenuation is temperature independent and proportional to the frequency. In this regime the velocity variations are slightly different. For both processes, the variations are proportional to the logarithm of the frequency and the temperature but the coefficient in front of $\ln T$ is characteristic of the process and provides a means to determine the dominant process. It is $2$ for the direct and $\frac{3}{2}$ for the Raman process. Finally it can be noted that in the $\omega T_1^m \gg 1$ regime the temperature dependence of the relaxation part of the attenuation is stronger for the Raman process than for the direct one. We used this difference to identify the dominant process above 10 K.

7. Conclusion. — Acoustic propagation in non-stoichiometric Na $\beta$-Al$_2$O$_3$ in the GHz frequency range and the 1.5-80 K temperature range is well described by the theory of two-level systems developed with success for amorphous materials. In that sense our work confirms previous specific heat, thermal conductivity, and dielectric measurements in $\beta$-Al$_2$O$_3$. Our principal results are:

i) the observation of a plateau in the acoustic attenuation at temperatures higher than 20 K which is attributed to the relaxation of the T.L.S. by the phonons in the regime $\omega T_1^m < 1$; this plateau is strong evidence for a distribution of T.L.S.-phonon coupling constants for T.L.S. of a given energy;

ii) the necessity to include a Raman relaxation process which becomes more efficient than the direct process near 10 K;

iii) the good agreement with experimental data found for the acoustic phase velocity variation when the relaxation of the T.L.S. by the Raman process plus an anharmonic contribution are included.

A complete set of acoustical experiments on an amorphous-type material, including attenuation and velocity changes at various frequencies over a wide
temperature range, has been performed and described successfully. Only the velocity change of one transverse mode is not explained in the framework of T.L.S. theory. We think that the study of nonstoichiometric \( \beta \)-alumina can provide not only information on the movement of the ions in that material and other superionic conductors, but also perhaps a microscopic description of the famous T.L.S., always present but never identified.

**Appendix.** — We wish to discuss here the behaviour of the integral

\[
I(v, \lambda, \mu) = \int_{r_m}^{1} dr \frac{r^{-\lambda}(1 - r)^{\mu+1/2}}{r + iv} \quad (A.1)
\]

when \( v \ll 1 \). This integral results from the more general distribution function \( P(A, \Delta_0) \) proposed in equation (15). In the article we limit ourselves to the particular case \( \lambda = 0 \) (see equation (30)). We develop

\[
(1 - r)^{\mu+1/2} = 1 - (\mu + 1/2) r + \cdots + a_{\mu} r^{\mu} + \cdots .
\]

It follows from the absolute convergence of this development for \( r_m \ll r < 1 \) that

\[
I(v, \lambda, \mu) = \int_{r_m}^{1} dr \frac{r^{-\lambda}}{r + iv} - (\mu + 1/2) \times
\]

\[
\int_{r_m}^{1} dr \frac{r^{\lambda-1} + \cdots + a_{\mu} r^{\lambda} + \cdots .}{r + iv} .
\]

We consider the general term

\[
J_q = a_q \int_{r_m}^{1} dr \frac{r^{q-\lambda}}{r + iv} . \quad (A.2)
\]

We assume \( \lambda \neq q \) (i.e. \( \lambda \) non-integer) and if \( r = v x \). \( J_q \) becomes

\[
J_q = a_q v^{q(\lambda - 1)} \int_{r_m/v}^{1/v} dx \frac{x^{q-\lambda}}{x + i} . \quad (A.4)
\]

We assume that \( r_m \) is so small that even when \( v \ll 1 \) we still have \( r_m/v \ll 1 \). On the other hand \( 1/v \gg 1 \). Therefore we can extend the integration limits to 0 and \( \infty \):

\[
J_q = a_q v^{q(\lambda - 1)} \int_{0}^{\infty} dx \frac{x^{q-\lambda}}{x + i} . \quad (A.5)
\]

This formula looks very much like the so-called reflection formula for the gamma function [34]

\[
\Gamma(s) \Gamma(1 - s) = \int_{0}^{\infty} dx \frac{x^{s-1}}{x + 1} = \pi \csc (\pi s) = \frac{\pi}{\sin (\pi s)} \quad (A.6)
\]

valid for \( s \) non-integer. The only difference is that in our case the pole in the complex plane is at \( z = -i \) instead of \( z = -1 \), but the method is similar. We integrate in the complex plane along the path shown in figure 11. We find:

\[
\int_{0}^{\infty} dx \frac{x^{n-1}}{x + i} = \pi \csc (\pi \lambda - q) \exp \left[ -i \frac{\pi (\lambda - q)}{2} \right]
\]

(\( A.7 \))

**Fig. 11.** — Integration path in the complex plane for the integral of equation (A.5). The cross indicates the pole at \( z = -i \).

and then

\[
J_q = -a_q v^{q-\lambda} \pi \csc (\pi q - \lambda) e^{+ix/2(q-\lambda)}
\]

\[
= -\frac{a_q}{2} \pi v^{q-\lambda} \left[ \csc \frac{\pi}{2} (q - \lambda) + i \sec \frac{\pi}{2} (q - \lambda) \right] \quad (A.8)
\]

\( I(v, \lambda, \mu) \) is obtained in summing all the terms of the type \( J_q \). If we are concerned with the dominant term we keep only the term of lowest order in \( v (v \ll 1) \) which is \( J_0 \). It reads:

\[
I(v, \lambda, \mu) = \frac{\pi}{2} v^{\lambda} \left[ \cos \frac{\pi}{2} \lambda - i \sec \frac{\pi}{2} \lambda \right] . \quad (A.9)
\]

The real part and the imaginary part of \( I(v, \lambda, \mu) \) are both proportional to \( v^{-\lambda} \), i.e. proportional to \( \omega T(\mu, E)^{-\lambda} \). As can be seen from equation (29) the first consequences of this result is that the velocity of sound is dispersive (it varies as \( \omega^{-\lambda} \)) and that the attenuation varies with the frequency as \( \omega^{1-\lambda} \). On the other hand, when the dominant process is such as

\[
\frac{1}{T^\alpha} = K_n T^\alpha F_n(\beta E) \quad (A.10)
\]

the velocity and the attenuation vary as \( T^{\alpha} \) (i.e. as \( T^{-1} \lambda \) when the Raman process dominates). When
$\lambda \neq 0$ the attenuation in the $v \ll 1$ régime depends on the temperature as $T^{m_0} :$ there is no plateau.
If $\lambda = 0$ we have

$$I(v, 0, \mu) = \int_{r_m}^{1} \frac{1}{r + iv} - (\mu + 1/2) \times$$

$$\int_{r_m}^{1} \frac{r}{r + iv} + \cdots + a_q \int_{r_m}^{1} \frac{r^q}{r + iv} + \cdots .$$

(A.11)

The first term is the largest one. Therefore :

$$I(v, 0, \mu) \simeq - \log iv = - \log v - i \frac{\pi}{2} .$$

(A.12)

In this case, the attenuation does not depend on the temperature and varies linearly with the frequency. The velocity varies as $- \ln \omega + n \ln T .

Now in the case where $\lambda = 0,$ there is another way to calculate the imaginary part of the integral $I(v, 0, \mu)$ (equation (A.1) where $\lambda = 0$) which helps to understand the physical meaning of the results. We start with

$$\lim_{v \to +0} \frac{1}{r + Iv} = \text{P.P.} \frac{1}{r} - i \pi \delta(r) .$$

As a consequence the imaginary part of the integral becomes :

$$\text{Im} [I(v, 0, \mu)] \simeq \frac{\pi}{2} \int dr \delta(r) (1 - r)^{m + 1/2} = \frac{\pi}{2} .$$

(A.13)

Two points must be underlined : i) the approximation is valid only if $r_m \ll v \ll 1$ because the excluded contribution to the integral (for $0 < r < r_m$) must be negligible as compared to the main contribution (for $r_m < r \ll 1$). ii) the weight of the Dirac distribution $\delta(r)$ is affected by a factor 1/2 because the integration is done only over the positive values of the variable $r.$ The physical meaning of this result is that the contribution to the acoustic attenuation is mainly due to the T.L.S. which have their parameter $r$ close to zero (in fact close to $r_m$ which is very small) or in other words, with the parameter $\Delta_0$ close to $\Delta_{m_0}.$ As a consequence, for these contribution T.L.S. we have

$$\omega T_1 \simeq \omega T_1^{m_0} r_m^{-1} = vr_m^{m_1} \gg 1$$

even if $\omega T_1^{m_0} = v \ll 1.$ Therefore, for these T.L.S. the hydrodynamic condition is not fulfilled. This explains why we do not obtain the usual dependence. In fact the existence of a plateau for the attenuation when $\lambda = 0$ and $v \ll 1$ is a general result when there is a distribution of the coupling strength. For instance let us assume that the relaxation time is such that :

$$\frac{1}{T_1(E, r, T)} = \frac{r^s}{T_1^n(E, T)}$$

$s > 0 .$$

(A.14)

(We do not claim that such a process exists, it is only a mathematical trick.) We deduce :

$$I(v, 0, \mu) = \int_{r_m}^{1} \frac{r^{-1}(1 - r)^{m + 1/2}}{1 + ivr^{-s}}$$

$$\int_{r_m}^{1} \frac{r^{m - 1}(1 - r)^{m + 1/2}}{r^s + ivr}$$

$$= \frac{1}{s} \int_0^1 dx \left( \frac{x^{1/2}r^{m + 1/2}}{x + iv} \right) .$$

(A.15)

and, if $s \neq 0$ we have

$$\text{Im} I(v, 0, \mu) = \frac{\pi}{2 s}$$

for $v \to +0.$

(A.16)

In this case too, we obtain a plateau if $s \neq 0,$ i.e. if there is a distribution of the coupling strength.
We have shown that the existence of the plateau does not depend on the expression for the relaxation time. Moreover, even the height of the plateau is completely independent of the relaxation process. What determines the plateau ? We know that it disappears when $\lambda \neq 0.$ This can be seen from

$$\text{Im} I(v, \lambda, \mu) = \text{Im} \int_{r_m}^{1} \frac{dr}{r + iv} r^{-\lambda} f(r) \simeq$$

$$\simeq \frac{\pi}{2} \int dr \delta(r) r^{-\lambda} f(r) .$$

(A.17)

The function $r^{-\lambda} f(r)$ must be finite and different from zero for $r \to 0.$ This is obtained if $\lambda = 0$ and if $f(0) \neq 0$ but finite. Therefore the existence of a plateau implies a condition on the distribution function : one must have

$$P(\Delta, \Delta_0) = \frac{\Delta}{\Delta_0} f(\Delta_0, \Delta)$$

(A.18)

with $f(\Delta_0, \Delta) \neq 0$ but finite for $\Delta_0 \to 0.$
References

[19] We thank B. SAPOVAL and H. ARRIBART for giving us the Fe-Al2O3 sample which was grown by Union Carbide; ROTHROCK, L. R., J. Cryst. Growth 39 (1977) 180.