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P. Doussineau, R.G. Leisure, A. Levelut, J.-Y. Prieur. Is non-stoichiometric crystalline Na β -alumina an ideal amorphous material? An ultrasonic answer. Journal de Physique Lettres, 1980, 41 (3), pp.65-68. 10.1051/jphyslet:0198000410306500 . jpa-00231723

HAL Id: jpa-00231723

<https://hal.science/jpa-00231723>

Submitted on 1 Jan 1980

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Classification
Physics Abstracts
43.35 — 62.65

Is non-stoichiometric crystalline Na β -alumina an ideal amorphous material? An ultrasonic answer

P. Doussineau, R. G. Leisure (*), A. Levelut and J.-Y. Prieur

Laboratoire d'Ultrasons (**), Université Pierre-et-Marie-Curie,
Tour 13, 4, place Jussieu, 75230 Paris Cedex 05, France

(Reçu le 22 octobre 1979, accepté le 3 décembre 1979)

Résumé. — Nous présentons les résultats de mesures de l'atténuation et de la vitesse d'ondes ultrasonores de fréquences voisines de 1 GHz dans de l'alumine β dopée au sodium pour des températures comprises entre 2 et 80 K. Nous avons observé deux régimes différents pour l'atténuation, l'un en $\omega^0 T^3$ à basse température, l'autre en ωT^0 à haute température, tandis que la vitesse passe par un maximum avant de décroître linéairement avec la température. Ces résultats sont en bon accord avec les prédictions de la théorie des systèmes à deux niveaux développée pour les matériaux amorphes. En ce sens l'alumine β semble être un *amorphe* idéal.

Abstract. — We report the results of ultrasonic attenuation and velocity measurements in the 1 GHz range in Na β -alumina and in the temperature domain 2-80 K. We observed two different behaviours for the attenuation, one varying as $\omega^0 T^3$ at low temperature, the other as ωT^0 at high temperature. The velocity goes through a maximum and then decreases linearly with the temperature. These results are found to be in good agreement with the predictions of the theory of two-level systems developed for amorphous materials. In that sense β -alumina appears to be an ideal *amorphous* material.

1. **Introduction.** — Non-stoichiometric sodium β -alumina and its isomorphs are interesting materials for several reasons. They are often called superionic conductors because of their exceptionally high ionic conductivity at elevated temperatures, but their low temperature behaviour is also striking. The specific heat [1, 2] of Li, Na, K, and Ag β -alumina exceeds the Debye specific heat by an amount which varies linearly with temperature while the thermal conductivity [3] of Li, Na, and Ag β -alumina depends on the square of the temperature. The dielectric behaviour is also unusual. In the case of Na β -alumina the dielectric constant varies logarithmically with temperature and the dielectric loss exhibits saturation effects [4]. Finally, the temperature dependence of the acoustic velocity in Na β -alumina has been found to be logarithmic [5]. These various low temperature properties are quite similar to those which have been observed in amorphous materials. β -alumina consists of spinel-

type blocks of aluminium and oxygen separated by mirror planes containing oxygen and the metal ions. Specific heat [1, 2], thermal conductivity [3], and dielectric measurements [6] indicate that these planes, which are highly disordered, are the origin of the amorphous-type behaviour.

We report here the results of ultrasonic attenuation and velocity measurements on Na β -alumina. These results, which indicate that in certain respects Na β -alumina is an ideal amorphous material, may be summarized as follows :

(i) In the lower temperature range ($T \leq 15$ K) the attenuation varies as $\omega^0 T^3$ where $\omega/2\pi$ is the ultrasonic frequency and T is the temperature. This attenuation law has been predicted [7] and observed [8] for amorphous materials, but has not previously been reported for a material such as β -alumina.

(ii) At somewhat higher temperatures the attenuation varies as ωT^0 . Although this behaviour was predicted [7] for amorphous materials, it has not yet been observed in these materials.

(iii) Above 10 K, the velocity decreases linearly with temperature. Such a velocity variation has also

(*) Permanent and present address : Department of Physics, Colorado State University, Fort Collins, Colorado 80523, U.S.A.

(**) Associated with the Centre National de la Recherche Scientifique.

been observed [9] in amorphous materials, but is not predicted by current theory. The logarithmic velocity variation observed at low temperatures [5] as well as points (i) and (ii) are in qualitative agreement with the theory of two level systems (T.L.S.) which has been developed for amorphous materials [10, 11].

The origin of the so-called *Two-level systems* in $\beta\text{-Al}_2\text{O}_3$ is certainly associated with the Alkali-ions. However, at least two microscopic models might be suggested. One model is that the interstitial atoms tunnel between equivalent positions (Mid-oxygen and/or Anti-Beever Ross one). Another is that the Alkali atoms tunnel between off centre positions as it has been proposed for the sylvanite [12]. We cannot choose between these two hypothesis.

A more detailed analysis of our experimental results will be given in a forthcoming article [13].

2. Experiments. — Measurements were made on melt-grown crystalline Na β -alumina [14] the 9.6 mm long sample was bonded to a corundum delay rod and longitudinal ultrasonic waves in the GHz range were propagated perpendicular to the c -axis. Standard

Fig. 1. — Temperature dependent part of the ultrasonic attenuation for four frequencies in Na $\beta\text{-Al}_2\text{O}_3$ as a function of the temperature on a log-log scale. The longitudinal waves propagated perpendicular to the c -axis. Estimated typical error bars are shown. They take into account the accuracy on one measurement at one temperature, the stability of the generator for a long time and the error when we compare curves at different frequencies.

pulse-echo techniques were used to measure the changes of the attenuation and of the velocity over the temperature range 2 K-80 K. The results for the attenuation measured at four frequencies are shown in figure 1, using logarithmic coordinates.

At the lowest temperature there is a region where the attenuation for all four frequencies falls on the same line within the experimental accuracy. The straight line through the data has a slope of 3, so that the attenuation is described in this temperature range by $\alpha \sim \omega^0 T^3$.

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 2. As can be seen, the frequency dependence is linear. Thus, at the highest temperatures, the dependence of the attenuation α on the frequency and temperature is given by $\alpha \sim \omega T^0$.

Fig. 2. — Attenuation of the plateau of figure 1, $\Delta\alpha = \alpha(30\text{ K}) - \alpha(2\text{ K})$ versus the ultrasonic frequency in Na $\beta\text{-Al}_2\text{O}_3$.

We have measured the ultrasonic velocity at 1 GHz and the results are shown in figure 3. The velocity increases with increasing temperature up to the maximum at about 7.5 K and decreases linearly with temperature above 10 K. A more detailed examination of the low temperature data indicates that the temperature dependence is in agreement with a logarithmic variation in the range 2 K-5 K. We have previously shown [5], using a different sample of Na β -alumina, that the temperature dependence is logarithmic in the range 0.1 K-5 K.

3. Theory. — We interpret our results in terms of the theory of T.L.S. proposed by Phillips [10] and Anderson-Halperin-Varma [11] for amorphous materials. This theory assumes that some unit of the amorphous material resides in a double well potential with an

Fig. 3. — Relative phase velocity change of 1.03 GHz longitudinal ultrasonic wave propagating perpendicular to the c -axis in Na β - Al_2O_3 .

energy splitting $2E$ which is related to the asymmetry energy 2Δ and tunnelling energy Δ_0 by

$$E = (\Delta_0^2 + \Delta^2)^{1/2}.$$

The exact nature of the T.L.S. is unknown, but they can be described [15] in terms of fictitious spins $S = 1/2$ which are coupled to the elastic strains ε by the hamiltonian

$$\mathcal{H} = \sum_i (G_x^i S_x^i \varepsilon + G_z^i S_z^i \varepsilon). \quad (1)$$

The coupling constants can be written in terms of the parameters of the double well as $G_x = 2br^{1/2}$ and $G_z = 2b(1-r)^{1/2}$ where $b = \partial\Delta/\partial\varepsilon$ and $r = (\Delta_0/E)^2$. In an amorphous material Δ and Δ_0 are assumed to have a wide distribution of values.

As Phillips has done [10] we use the following distribution function

$$P(\Delta, \Delta_0) = \frac{A}{\Delta_0} \quad (2)$$

for

$$0 \leq \Delta \leq \Delta_1 \\ \Delta_m \leq \Delta_0 \leq \Delta_M,$$

and $P(\Delta, \Delta_0) = 0$ otherwise. A is a constant to be determined by normalization. In terms of the parameter E and r the distribution function becomes

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

and zero.

The first term in the hamiltonian (1) describes resonant transitions between the two levels. In our experimental conditions the resonant attenuation is negligible. Then we consider only the resonant contribution to the velocity which is given by

$$(\Delta v/v)_{\text{res}} = C \ln(T/T_0) \quad (3)$$

where T_0 is a reference temperature. We have used the dimensionless coupling coefficient

$$C = (n_0 G_x^2 / 4 \rho v^2) = (N A b^2 / 2 \rho v^2)$$

where G_x^2 is a mean value, n_0 is the density of states of the T.L.S., ρ is the density of the material, v is the velocity of sound, and N is the number of T.L.S. per unit volume. Equation (3) is only valid for $\hbar\omega \ll kT$.

The second term in the coupling hamiltonian describes a modulation of the energy level splitting by the acoustic strain and is responsible for a relaxation attenuation. The corresponding change $\delta c(\omega)$ in the complex elastic constant may be written

$$\delta c(\omega) = - (1/2) N A b^2 \beta \int dE \text{sech}^2 \beta E \times \\ \times \int_{r_m}^1 \frac{dr(1-r)^{1/2}}{r + i\omega T_1^m} \quad (4)$$

where $r_m = (\Delta_m/E)^2$. Here, T_1^m is the minimum T.L.S.-lattice relaxation time for T.L.S. of a given energy. We assume the direct process for the relaxation time T_1 in which case we may write [7] :

$$\frac{1}{T_1} = \left(\frac{\overline{b^2}}{v^5} \right) \frac{4rE^3}{\pi\rho\hbar^4} \coth \beta E \quad (5)$$

where $(\overline{b^2}/v^5)$ is an *ad hoc* average value over the wave-vector directions and the polarizations. T_1^m is obtained by setting $r = 1$ in equation (5). The relaxation contribution to the attenuation and velocity may now be obtained from $\delta c(\omega)$. The results are

$$\alpha_{\text{rel}} = \frac{\pi^3 C k^3 T^3}{24 \rho v \hbar^4} \left(\frac{\overline{b^2}}{v^5} \right) \quad (6a)$$

$$(\Delta v/v)_{\text{rel}} = \frac{16 \pi^4 C k^6 T^6}{315 \rho^2 \hbar^8 \omega^2} \left(\left(\frac{\overline{b^2}}{v^5} \right) \right)^2 \quad (6b)$$

for low temperatures where $\omega T_1^m \gg 1$ and

$$\alpha_{\text{rel}} = C \pi \omega / 2 v \quad (7a)$$

$$(\Delta v/v)_{\text{rel}} = (1/2) C \left(\ln \frac{\omega}{\omega_0} - 3 \ln \frac{T}{T_0} \right) \quad (7b)$$

for high temperatures where $\omega T_1^m \ll 1$. ω_0 is a reference frequency.

The results for $\omega T_1^m \gg 1$ are well known [15]. For $\omega T_1^m \ll 1$ they have not yet been observed. We note that for this second case the magnitudes of the predicted effects do not depend on the relaxation process.

4. **Discussion.** — Clearly our attenuation results can be explained by the relaxation of the T.L.S. In the temperature range 5-15 K, the $\omega^0 T^3$ law can be ascribed to the relaxation of the T.L.S. by a one-phonon process in the case where $\omega T_1^m \gg 1$ (Eq. (6a)). At higher temperatures the ωT^0 law is interpreted as the relaxation attenuation in the regime $\omega T_1^m \ll 1$ (Eq. (7a)) which is independent of the relaxation process provided there is a distribution of the coupling strength.

We now make a quantitative comparison between theory and experiment. From the logarithmic velocity change given by equation (3) and from the plateau of the attenuation given by equation (7a) we deduce two values for the coupling constant c_1 of the longitudinal wave,

$$(3.6 \pm 0.4) \cdot 10^{-5} \quad \text{and} \quad (6.8 \pm 0.4) \cdot 10^{-5}$$

respectively. The discrepancy between the two values is much larger than our accuracy, but we think that some modifications of the distribution function $P(\Delta, \Delta_0)$ can explain such a difference [13].

We previously measured the ultrasonic velocity in a different specimen of Na β -alumina over the temperature range 0.1-15 K [5]. In the temperature range where the two experiments overlapped the results are similar. However the coefficient C is about 40 % greater in the previous sample. As the two samples were grown by different methods [16] the different results may reflect a different amount of disorder in the two specimens.

In figure 1 it seems that for the curve at the highest frequency (1 950 MHz) there appears on the plateau a small increase of the attenuation above 50 K. We attribute this effect to the usual Akhiezer attenuation in crystalline insulators [17]. Its ω^2 dependence prevents its observation at lower frequency.

From the data in the T^3 temperature region (Fig. 1) we can determine (b^2/v^5) using equation (6a). Taking $C = 6.8 \times 10^{-5}$, we find $3.2 \times 10^{-54} \text{ g}^2 \text{ cm}^{-1} \text{ s}$

which is an acceptable value knowing b_1 and the elastic constants of Na β -Al₂O₃. For a more complete quantitative interpretation in this temperature region we need the value of coupling constants for the different modes.

We can compare our results to the thermal conductivity [3] and dielectric constant [6] measurements of Anthony and Anderson. From their thermal conductivity measurements [3] we find for the coupling constant C_1 , 10×10^{-5} and from their dielectric constant [6], 21×10^{-5} , for the T.L.S. with energy around 1 K. Actually these values are obtained through average calculations over different modes and we can compare only the orders of magnitude. Therefore they are in general agreement with our values 3.6×10^{-5} and 6.8×10^{-5} .

Not accounted for in the above analysis is the linear decrease of the velocity with increasing temperature after the maximum. The attenuation measurements show that in this temperature range, the condition $\omega T_1^m \ll 1$ is fulfilled. Therefore the predicted velocity decrease (Eq. (7b)) is logarithmic and weaker than that observed. Very recently it has been claimed that an appropriate modification of the distribution function can account for this linear decrease [18]. This point asks for a careful analysis beyond the scope of this letter and we shall discuss it in a forthcoming paper [13].

5. **Conclusion.** — With the exception of the high temperature velocity measurements, our ultrasonic results on Na β -alumina are well-accounted for by the theory of T.L.S. developed for amorphous materials. In a certain sense β -Al₂O₃ serves as a better model for the theory than do the true amorphous solids : it appears as an *ideal* amorphous material. For example, the high temperature plateau of the attenuation has not been observed in any amorphous materials, probably because it is obscured by another effect.

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