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FURTHER STUDY OF THE "GLASSY" LOW-TEMPERATURE PROPERTIES OF IRRADIATED CRYSTALLINE QUARTZ : NEUTRON AND ELECTRON IRRADIATION

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Abstract :

Recently it has been shown that a quartz crystal after light fast neutron irradiation shows low temperature hypersonic properties which are similar to those found in glasses although the sample was still crystalline. Additional measurements have been carried out in the neutron-irradiated sample and a sample irradiated with high energy electrons has also been investigated. (Fast neutron dose 6×10^{18} n/cm^2, 2 MeV electron dose 3×10^{19} e/cm^2).

A magnetic field up to 1.5 T was found to have no influence in the hypersonic saturation behaviour of the neutron-irradiated sample (9 GHz, 1.65 K) and thermal conductivity measurements are consistent with a number of two level systems (2 LS) an order of magnitude lower than in vitreous silica as found before.

Low temperature hypersonic measurements as a function of acoustic intensity and temperature as well as thermal conductivity measurements give no evidence for the presence of 2 LS in the electron irradiated sample. Considering the damage created in both samples this indicates that 2 LS are probably not related to point defects.

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FURTHER STUDY OF THE "GLASSY" LOW-TEMPERATURE PROPERTIES OF IRRADIATED CRYSTALLINE QUARTZ : NEUTRON AND ELECTRON IRRADIATION [x]

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Résumé :

On a récemment mis en évidence qu'un cristal de quartz irradié avec une faible dose de neutrons présentait des propriétés hypersonores à basse température similaires à celles qu'on observe dans les verres, bien que l'échantillon soit encore cristallin après l'irradiation.

Des mesures complémentaires ont été réalisées sur le quartz irradié aux neutrons et on a également examiné le comportement d'un échantillon irradié aux électrons (dose de neutrons rapides : $6\ 10^{18}$ n/cm^2 ; dose d'électrons de 2 MeV : $3\ 10^{19}$ e/cm^2).

On a trouvé qu'un champ magnétique (de 0 à 1,5 T) n'avait aucune influence sur la saturation hypersonore de l'échantillon irradié aux neutrons. L'expérience a été faite à 1,65 K à la fréquence de 9 GHz. Des mesures de conduction thermique réalisée sur le même échantillon permettent d'estimer une concentration de systèmes à deux niveaux environ dix fois moindre que dans la silice vitreuse, ce qui est cohérent avec les résultats des mesures hypersonores.

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Des mesures hypersonores à basse température en fonction de la température et de l'énergie acoustique incidente ainsi que des mesures de conduction thermique, n'ont pas permis de mettre en évidence la présence de systèmes à deux niveaux dans l'échantillon irradié aux électrons. En comparant les défauts créés dans les deux échantillons, ces résultats tendent à indiquer que les défauts ponctuels ne sont pas liés aux systèmes à deux niveaux.

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I - INTRODUCTION -

The low temperature anomalous thermal, acoustic and dielectric properties of amorphous materials have been studied extensively during the last decade. They are accounted for by assuming the existence of some sort of low energy excitations. These excitations can be succesfully described as systems in which a tunneling process between two nearly degenerate energy levels, separated by an energy E, can occur ; or more simply as two-level systems (2LS). The roughly linear contribution to the specific heat observed in all glasses (except As) at low temperatures is explained as resulting from a nearly constant density of states of these 2 LS. The strong interaction between these low energy excitations and phonons leads to a very small thermal conductivity and unusual effects in the propagation of elastic waves (saturation). However, the microscopic nature of the tunneling process i.e. the tunneling entity is not yet known.

The anomalies mentioned above were found in a variety of amorphous materials and were considered as intrinsic to the amorphous state. Recently it has been seen however that a quartz crystal, after light fast-neutron irradiation shows similar hypersonic properties as glasses (Laermans, 1979). The further observations of phonon echoes in the same sample showed that the observations could be accounted for by a number of 2LS which is roughly one order of magnitude less than that in glasses and that the main parameters, as there are, the coupling constant M, the relaxation times T_1 and T'_2 are remarkably similar to those found in the glass (Golding et al.,1979). Therefore it turns out that the study of a defective quartz crystal is an interesting tool for the study of the anomalous low temperature dynamic properties of glasses.

The purpose of the work reported here was to extend the study of defective quartz crystals. 9 GHz hypersonic attenuation measurements, in and without a magnetic field and thermal conductivity measurements were carried out in a neutrons-irradiated and an electron irradiated sample. While neutron-irradiation is known to cause point defects and clusters of defects (Berman, 1951; Klemens, 1951), electron-irradiation causes only single defects. Since the number of single defects in both samples must be roughly the same for the used irradiation doses, such experiments should clarify the question wether 2LS are related to point defects. In this way, one might be able to turn down gradually the possible defects which cause 2LS.

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II - THEORY -

II-1-Thermal conductivity

At very low temperatures, the dominant interactions between the 2LS and acoustic waves is the direct process, e.g. the absorption or emission of a resonant phonon.

At thermal equilibrium and if we suppose only direct scattering, the mean free path of the phonon of frequency ω and polarization α is then given by (Hunklinger and Arnold, 1976)

$$l^{-1}(\omega,\alpha) = \frac{\Pi n_0 M^2 \omega}{\rho v^3_\alpha} \tanh \frac{\hbar\omega}{kT} \qquad (1)$$

In this expression, n_0 is the constant density of states of the 2LS and M is the coupling constant for the resonant interaction.

From the equation (1) we can deduce the relaxation time

$$\tau(\omega,\alpha) = \frac{\rho v^2 \alpha}{\Pi n_0 M^2 \omega} \coth \frac{\hbar\omega}{kT} \qquad (2)$$

For thermal conductivity analysis, it is convenient to simplify the summation on the three phonon polarization taking a mean velocity v given by

$$\frac{3}{v^3} = \frac{1}{v_L^3} + \frac{2}{v_T^3} \qquad (3)$$

We obtain

$$\tau(\omega) = \frac{\rho v^2}{\Pi n_0 M^2 \omega} \coth \frac{\hbar\omega}{kT} \qquad (4)$$

We can replace this expression in the equation giving the thermal conductivity calculated in the Debye approximation (Berman, 1976).

$$K(T) = \frac{k}{2\Pi^2 v} \left(\frac{k}{\hbar}\right)^3 T^3 \int_0^{\Theta/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} dx \qquad (5)$$

Where we have done the usual substitution $x = \frac{\hbar\omega}{KT}$.

Θ is the Debye temperature

The replacement of $\tau(x)$ by the expression of the equation (4) gives :

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$$K(T) = \frac{k}{2\Pi^{2}\ v} \left(\frac{k}{h}\right)^{3} T^{3} \left(\frac{v\rho\ v^{2}}{\Pi n_{o}\ M^{2}.T} \quad \frac{\hbar}{k} \right) \int_{o}^{\Theta/T} \frac{x^{3}\ e^{x}}{(e^{x} - 1)^{2}} \tanh x\ dx \qquad (6)$$

This expression of K(T) demonstrates the T^2 law which is characteristic of the glasses at low temperature.

Furthermore we see that for a given T, in the T^2 region, the value of K(T) is inversely proportional to the number n_o of the 2LS. A consequence is that by comparison of the K(T) curves of neutron irradiated samples at different doses, it will be possible to evaluate the number of created 2LS.

II-2-Acoustical properties

The interaction of the 2LS with an acoustic wave is twofold : the resonant attenuation due to the direct process and a relaxation attenuation. At high acoustic intensities the absorption is intensity dependent because the upper level becomes more and more populated ; it is given by Hunklinger and Arnold, 1976 :

$$\alpha_{res} = \frac{n_o\ M^{2}\ \Pi}{\rho\ v^{3}} \ \frac{\omega}{\sqrt{1 + J/J_c}} \ \tanh \frac{\hbar\omega}{2kT} \qquad (7)$$

J is the acoustic intensity and J_c is the critical intensity at which saturation becomes noticeable. Since the energy of the ultrasonic phonon is small compared to kT, tanh $\frac{\hbar\omega}{2kT}$ can be replaced by $\frac{\hbar\omega}{2kT}$:

$$\alpha_{res} = \frac{n_o\ M^{2}\ \Pi}{\rho\ v^{3}} \ \frac{\omega^{2}}{T} \qquad (8)$$

The relaxation attenuation is due to another process : travelling through an ensemble of two-level systems the sound wave disturbs their thermal equilibrium and the systems try to relax into a new equilibrium which is re-established via the emission and absorption of thermal phonons.

The attenuation due to this interaction is in the low temperature limit $\omega\tau >> 1$ given by Hunklinger et al, 1976

$$\alpha_{rel} = n_o\ D^{2} \left(\frac{M_1}{v_1^{5}} + \frac{2\ M_t^{2}}{v_t^{5}} \right) \frac{\zeta(4{,}05)\ T^{3}\ k^{3}}{32\Pi\ \rho^{2}\ h^{4}\ v^{3}} \qquad (9)$$

Where $\zeta(4,05)$ is the Rieman zeta function whose numerical value is 97.38. D is the coupling constant for the relaxation process. The indices l and t indicate the longitudinal and the transverse mode.

III - EXPERIMENTAL RESULTS -

The experiments reported in this paper have been performed on three samples noted A, B and C. A and B are natural brazilian X cut quartz crystals provided by the same supplier. C is a borosilicate glass.

The sample A is fast neutron irradiated ($E \sim 1$ MeV) with a dose of 6.10^{18} neutrons/cm^2 and was previously used by Laermans for hypersonic experiments (Laermans, 1979). The irradiation was done in the Reactor Centrum "Studiecentrum voor Kernenergie" (SCK) in Mol (Belgium). The sample which is 8,4 mm long and has a diameter of 3 mm was maintained at about 60°C during the irradiation.

The sample B was irradiated with 2 MeV electrons at the Service des Accélérateurs of the Centre d'Etudes Nucléaires de Grenoble (CENG), France. The sample is 6 mm long, its diameter is 3 mm. It received a dose of 3.10^{19} e/cm^2 and was rotated to ensure an uniform irradiation. Furthermore it was air-cooled and maintained at about 50°C during the irradiation.

After the irradiation, the sample appeared to be more smoky than the neutron irradiated one which indicates the presence of a greater number of color centers.

The sample C is in the as received state, its length is 6 mm and its diameter is 3 mm.

III-1-9 GHz measurements

Using the sample A we have done an experiment analogous to the one reported previously by Laermans (1979). The figure 1 shows the result : we have plotted the attenuation in the crystal (measured between the second and the third echo) as a function of the attenuation in db of the input acoustic power. In the saturated zone, the attenuation value is 7 db which corresponds roughly to 4 db/cm. The temperature was 1.5 K.

We have furthermore applied a magnetic field of 0 to 15 kOe along the axis of the sample and, in a second experiment, doing a 45° angle with this axis. In both cases, we have not found a variation of the saturation value or of the temperature dependent relaxation attenuation.

Measurements of hypersonic attenuation as a function of the acoustic intensity were also carried out in sample B, at 1.65 K but down to the lowest intensities no change was seen. Also the measurements as a function of temperature did not reveal a noticeable temperature dependence in the range 1.65 K to 4,2 K. This limits the possible effect to less than 0,2 db/cm which was the sensitivity of the apparatus of the measurement.

For this sample, we have also applied a magnetic field of 15 kOe along the axis and at 45° of it. This measure was done at 4.2 K and at 1.6 K and in both cases we have seen no effect.

The measurements with a magnetic field have not revealed APR lines and this leads us to think that there are not strongly coupled paramagnetic defects in both samples A and B.

III-2-<u>Thermal conductivity</u>

The thermal conductivity measurements on A are reported in figure 2. At 10 K we observe a maximal conductivity of 3 10^{-2} W/K.cm. The maximum is large, nearly a plateau. In figure 2, we have plotted the experimental results of Zeller and Pohl(1971) in virgin quartz. We observe that our curve is situated well below this one,that is irradiation has damaged the crystal and created defects lowering the thermal conductivity.

This result is similar with that of Berman (1951) who studied the variation of thermal conductivity with the neutron dose. Our experimental curve corresponds roughly to that obtained by Berman for a dose of 3 10^{19} n/cm^2. This dose is about 5 times larger as in our experiment but the comparison is not very significant because of the experimental differences (for instance the energy of neutrons is not given by Berman). We note that in our experiment the lower temperature is 1.4 K whereas it was about 3 K for Berman's one.

Results of the measurements on sample B are plotted on the same figure. The maximal conductivity is 2 W/K.cm at 15 K and the curve is above that on sample A. That is coherent with the fact that the sample was less damaged by electron irradiation than by neutrons. The maximum is however not so broad as in the case of curve A and is lower than that is a virgin sample. The curve corresponding to the sample C (see fig.2) shows the plateau which is characteristic for the glasses. The shape of the curve is similar to that obtained by Zeller et Pohl (1971) for vitreous silica.

IV - DISCUSSION -

IV-1-Neutron irradiated quartz

Let us first consider the results in neutron irradiated quartz. The fact that the resonant attenuation is not influenced by a magnetic field up to 1.5 T gives evidence that the defects seen are not paramagnetic defects.

This is consistent with the results of Stephens (1976) who finds that the excess of specific heat due to Fe ions in borosilicate scales with their concentration. However there still remains an excess of specific heat compared to the crystal which is not influenced by the magnetic field and therefore probably intrinsic to the glassy state.

The thermal conductivity measurements which are partly carried out in the same temperature range as those from Berman (1951) but extended to lower temperatures, are consistent with Berman's results. The maximum found in crystals at $\simeq$ 10 K is very much reduced and is almost only a bump. The plateau at 10 K which is so typical for amorphous materials is almost reached. At lower temperatures the curve tends to the T^2 observed in glasses. From the values at lower temperatures an estimation of the number of 2LS can be done. Taking into account that the coupling constant M is similar to that in vitreous silica (Golding et al. 1979) it is seen that the number of 2LS is roughly an order of magnitude smaller than in vitreous silica which is in agreement with earlier measurements (Golding et al.1979).

The thermal conductivity measurements give further evidence that the "glassy" properties observed here are not due to the Al linked electronic center observed in ultrasonic and thermal measurements by Saint-Paul, Chaussy, Wasim and coworkers (Saint-Paul et al. 1978a,1978b ; Wasim et al. 1979; J. Chaussy et al.,1979). While it was found before that acoustic measurements give different results (Laermans, 1979) it is now seen that the thermal conductivity is also different in neutron and γ-irradiated quartz. In the case of neutron irradiation the peak at about 10 K is much more reduced than after γ-irradiation.

Since it is known that quartz upon heavy neutron irradiation ($2\times10^{20} n/cm^2$) vitrifies one might wonder whether the observed properties are note due to vitrification of the sample. This is not the case for the lightly irradiated sample ($6 \times 10^{18} n/cm^2$) for different reasons. The thermal conductivity behaviour is not the same as in vitreous silica and it is still an order of magnitude higher. Furthermore it is known that the sample is still long range ordered (Laermans, 1979, Golding et al.1979). For instance, the hypersonic waves are generated by surface excitation of the sample itself. Another interesting point to consider is that even heavy neutron irradiation of quartz does not render the crystal in a phase which is the same as vitreous silica. The density is higher by 14 % (Lell et al.1966) and it is know that upon heavy irradiation both the crystalline and the vitreous form of SiO_2 evolve to a common phase which is disordered but different from vitreous silica. This means that if "amorphous" regions would be present in the hightly irradiated quartz they would certainly be different from vitreous silica. In addition, the irradiated crystal contains 5 x 10^{19} unpaired electron spins per cm^3 (from magnetic susceptibility measurements, Vandenbosch), while vitreous silica does not show any presence of such spins.

Taking into account the above considerationsit is interesting to look at the observations in neutron irradiated vitreous silica. The irradiation is found to reduce the number of 2LS. This is found in ultrasonic saturation experiments (Laermans et al.1977) as well as in measurements of the specific heat (Smith et al.1978). This means that neutron irradiation introduces the anomalies in the crystal while it reduces them in the glass.

IV-2-Electron-irradiated quartz

The results on the neutron irradiated quartz give evidence that the 2LS are not related to electronic centers as created by ionizing radiation and therefore that they are probably the result of structural changes in the crystal. The purpose of the measurements on the electon-irradiated sample was to pin down further the possible defects related to 2LS in glasses. Some authors state that neutrons cause single defects and clusters of defects (for references see Billington et al. 1966). Electrons also cause structural changes but they only give rise to single defects. According to Billington et al.(1966) the energy of the electrons is too low to cause secondary displacements and therefore complex localized regionsof damage that result from the displacement cascade are excluded. The Frenckel defects are randomly distributed throughout the affected portion of the specimen. According to Klemens (1951) who gave an explanation of Berman (1951) thermal conductivity measurements on neutron-irradiated quartz the number of single defects for a neutron dose of 2 x 10^{18} cm^{-2} is of the order of 10^{19} cm^{3}.

The displacement threshold being 0,3 to 1 MeV and the displacement cross section 10 to 100 barn (Billington et al.,1961), an electron dose of $3 \times 10^{19}/cm^2$ causes a number of single defects in our sample of the same order of magnitude as in our neutron irradiated crystal.

If the number of single defects is the same in the electron and neutron irradiated specimen (we have to stress the fact that only rough estimates are possible) the absence of any measurable saturation in the hypersonic attenuation would indicate that the single defects are not related to the 2 LS which are believed to cause the acoustic anomalies in the neutron irradiated sample. The fact that no saturation could be observed reduces the possible number of such 2 LS present in the electron irradiated sample to at least 10 times less than in the neutron irradiated sample. This is also consistent with an estimate made according to the measurements of the hypersonic attenuation as a function of temperature . Indeed, since no change of α has been seen between 1.65 K and 4.2 K it must be smaller than 0.2 dB (experimental accuracy) which means that it is also at least an order of magnitude smaller than in the neutron irradiated sample. Considering all these estimates we have to keep in mind however that it was always supposed that the coupling constants are the same as in the neutron irradiated quartz, this means as in the glass (Golding et al., 1979).

The thermal conductivity measurements are consistent with the hypersonic observation and the considerations above : they give no evidence for the presence of 2 LS in the electron irradiated sample.

All these observations are also consistent with the results of Lohneysen et al.(1978) who found no change of the low temperature specific heat of electron irradiated vitreous silica. However it has to be noted that they used an electron dose which was 3 to 10 times lower.

FIGURE CAPTIONS

FIG. 1 Hypersonic saturation effect in fast neutron irradiated quartz crystal.

FIG. 2 **Thermal conductivity of quartz crystal of neutrons and electron irradiated quartz and borosilicate glass**

V : quartz crystal (after Zeller and Pohl, 1971)

A : fast neutron irradiated quartz energy of 1 MeV, dose of 6 10^{18} n/cm^2

B : electron irradiated quartz (energy of 2 MeV, dose of 3 10^{19} e/cm^2)

C : borosilicate glass

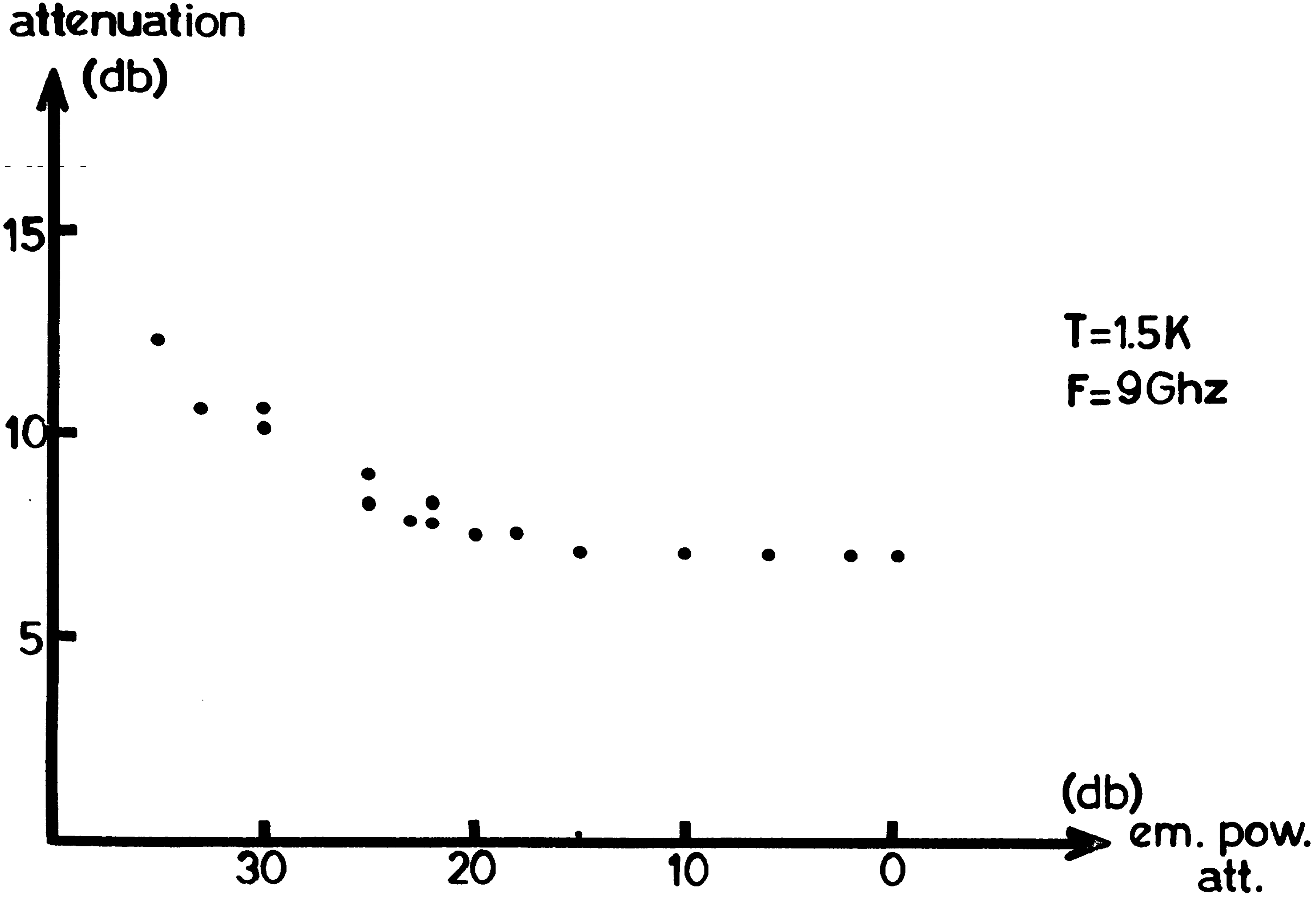

FIGURE 1

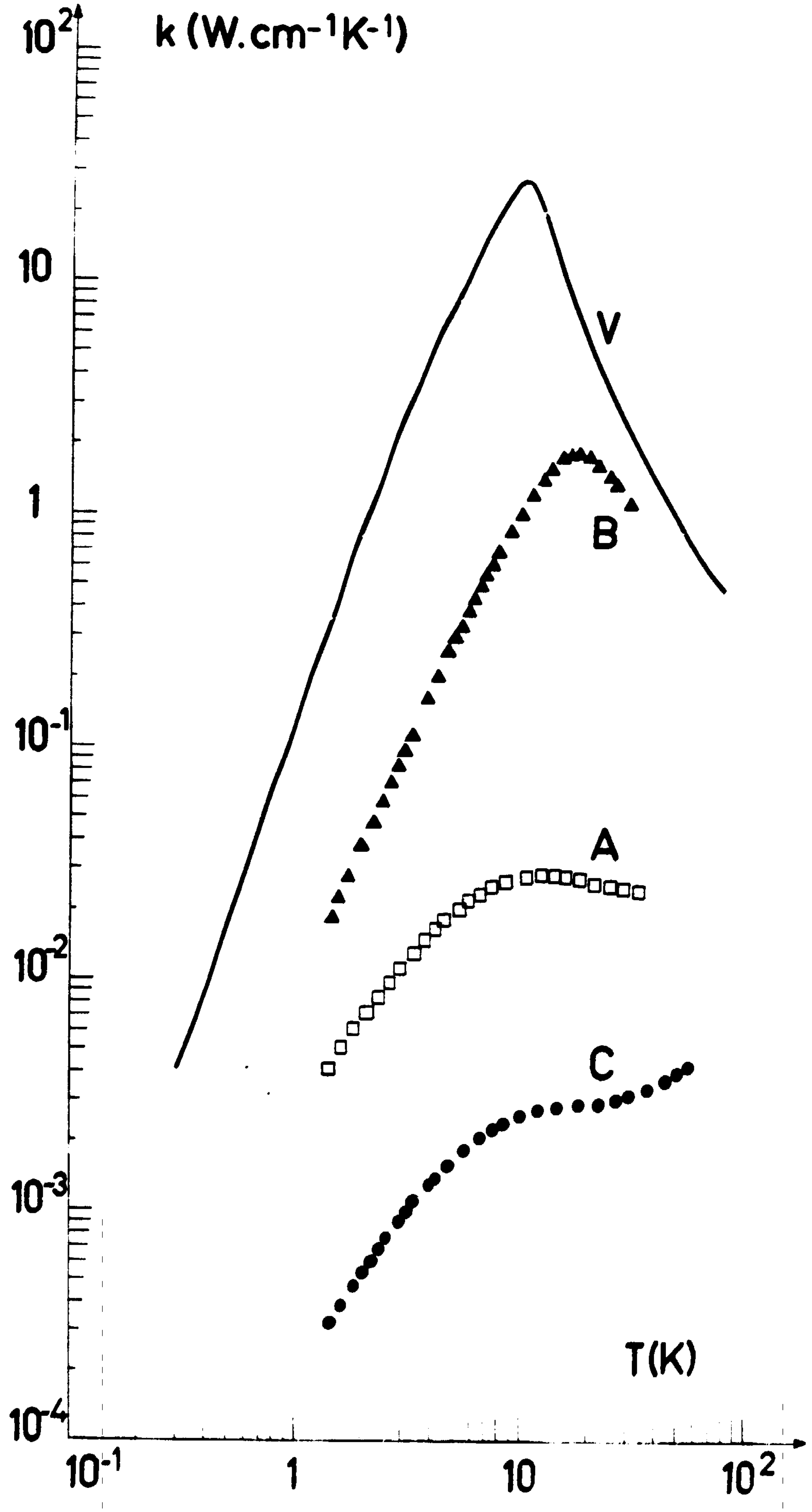

FIGURE 2

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