

A NEW INVESTIGATION OF DIELECTRIC RELAXATION PROCESSES IN SMOKY QUARTZ CRYSTALS

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Synopsis

Dielectric loss measurements on smoky quartz crystals over a wide frequency and temperature range (200 Hz–2.5 MHz and 20.4–160°K) showed, besides the well-known relaxation process at low temperatures, also a new relaxation mechanism, which becomes dominant above 100°K. There are strong arguments that both processes are due to the same type of colour centres. The rate theory in its simplest form cannot be held. The experiments are discussed with the help of Sussmann's theory of intermediate states including tunnelling processes.

The deviations of the $\tan \delta$ curves from the theoretical Debye curve, due to a spread in relaxation times, were studied. At low temperature there appeared to be a uniform relation between the measured mean value $\langle \tau \rangle$ and the experimentally determined spread τ_H/τ_L , defined by the Fröhlich distribution function $g(\tau) \propto \tau^{-1}$ for $\tau_L < \tau < \tau_H$. The upper limit τ_H has, at constant temperature, a nearly constant value for various samples. The lower limit τ_L , however, varies by more than a factor 10. At high temperature only a very small spread in τ values was found.

I. *Introduction.* Several experimental and theoretical studies have been made in the field of dielectrics in order to get more insight into the processes which lead to the relaxation of permanent electric dipoles in solids and the interactions which determine the temperature and frequency dependence of the dielectric function.

In this paper we will report on the behaviour of the electric dipoles, associated with the colour centres in smoky quartz. The optical and magnetic properties of these colour centres have been studied by many authors in detail¹⁻⁶). Stevels and Volger⁷) reported the first dielectric measurements. They measured dielectric losses of the Debye type in the temperature range from 16–70°K at low frequencies on both natural smoky quartz and X-irradiated synthetic quartz crystals. They assumed that the electrons trapped at the interstitial ions, thus forming colour centres, also give rise to the high dielectric losses, found in this temperature range. These electrons in association with their trapping centres, which are effectively positively charged, obviously form electric dipoles which at each instant may point

into a number of possible directions, having equal energy. The substitutional aluminium ions, each having trapped a hole, contribute only to the loss angle at higher frequencies. The experimental results were in reasonable agreement with the rate theory which assumes that the particle (in this case the trapped electron) has two or more eccentric equilibrium positions, which correspond to minima of a potential function, and that the particle can make the transition from one equilibrium position to another, provided it has sufficient energy to surmount the potential barrier. Stevels and Volger used the the well-known formula for the relaxation time τ connected with such transitions

$$\tau = \tau_0 \exp(E/kT)$$

where E is the height of the potential barrier. They found $E = 7.5$ meV for the colour centres in smoky quartz. In the usual rate theory $(\tau_0)^{-1}$ should be about the frequency of vibration of the particle in the potential well. For τ_0 an unusually high value was found: $\tau_0 = 5 \times 10^{-7}$ s.

Taylor and Farnell⁶⁾ reported briefly on analogous measurements, but now also below 16°K. They found another loss mechanism, which becomes dominant at lower temperatures, with

$$E = 1 \text{ meV} \quad \text{and} \quad \tau_0 = 6 \times 10^{-5} \text{ s.}$$

They suggest that with this second loss mechanism the same dipoles are involved, because the strength of the dipoles was of the same order of magnitude as found by Stevels and Volger. It seemed thus possible to explain these experiments, like many other dielectric investigations, with the aid of the rate theory. Fröhlich *e.a.*⁶⁾, however, disputed this simple theory.

Recently, Sussmann⁹⁾ gave a quantum mechanical analysis of tunnelling processes of ions in solids as a decisive part of the relaxation mechanism. His result was

$$\langle \tau \rangle^{-1} = \sum (\tau_i)^{-1}$$

τ_i has the form $A \cdot T^{-x}$ with $x = 0, 1, 2, 4$ or 7 for phonon-induced tunnelling processes at lower temperature. On the other hand, τ_i takes the form $B \cdot \exp(E/kT)$ for processes at higher temperature where transitions via intermediate states are important, which makes certain aspects of the rate theory applicable again. Bosshard, Dreyfus and Känzig¹⁰⁾ recently observed a relaxation behaviour of hydroxyl-doped potassium chloride at very low temperature, a fact that is well explained by this theory.

It seems very likely that also our dielectric measurements on smoky quartz crystals in the temperature region from 20 to 160°K and in a wide frequency range (to 2.5 MHz) may be discussed in terms of Sussmann's theory.

II. *Experimental technique.* The dielectric relaxation time τ can be found

from the expression for the loss angle δ

$$(T \cdot \tan \delta)^{-1} \propto \omega\tau + (\omega\tau)^{-1}$$

valid for Debye type relaxation.

$\tan \delta$ was measured as a function of both frequency and temperature. In both cases the function $T \cdot \tan \delta$ has its maximum when $\omega\tau = 1$. From the frequency or the temperature where the maximum is reached we determined τ as function of T .

A natural smoky quartz crystal*) was cut into thin samples perpendicular to the C axis. The area of the samples was about 1 cm²; the thickness varied from 0.1 to 0.2 mm. The surfaces were polished with very fine carborundum. Silver electrodes were evaporated onto them or painted with colloidal silver paint (Leitsilber 200, Degussa). However, no difference in the results of these two methods could be found.

The measuring cell was mounted in a small Joule-Thomson hydrogen liquefier cryostat**). The cooling power of this small cryostat was about 1 calorie per second, sufficient to cool down the measuring cell from 80 to 20°K in twenty minutes or to produce about a quarter of a liter liquid hydrogen per hour.

The temperature was measured with the help of copper wire resistance or carbon resistance thermometers, with an accuracy of 1%. A thermostat stabilized the temperature within 1% over a few hours.

All $\tan \delta$ measurements were performed on a General Radio Capacitance Bridge, type 716 C, using a substitution method, applying a switch at the bottom of the measuring cell, close to the crystal. The accuracy of the $\tan \delta$ values obtained was about 1×10^{-4} . The measuring A.C. electric voltage was about 10 volts at the specimen, i.e. 500 to 1000 volts/cm field strength in the crystal.

From the maximum value of $\tan \delta (= \tan \delta(\omega_m))$ one can obtain the dipole strength P , using the relation⁷⁾

$$\tan \delta(\omega_m) = \frac{4\pi}{3\epsilon} \frac{N \cdot P^2}{k \cdot T} \left(\frac{\epsilon + 2}{3} \right)^2 \quad (1)$$

The dipole concentration N can be estimated from the concentration of the impurities in the crystal***). The found dipole strength P is about 4 Debye units (= $4 \cdot 10^{-18}$ e.s.e.).

III. *Experimental results.* Fig. 1 shows two typical curves of $\tan \delta$ versus frequency on reduced scales, measured at the temperatures indicated. Fig. 2

*) This quartz crystal is of Ukrainian origin, the same crystal that has been studied by Stevels and Volger⁷⁾.

***) The authors are indebted to J. van Suchtelen for the design and the setup of this cryostat.

***) The chemical analyses were performed under the supervision of Dr. N. W. H. Addink, Philips Research Laboratories, Eindhoven, The Netherlands.

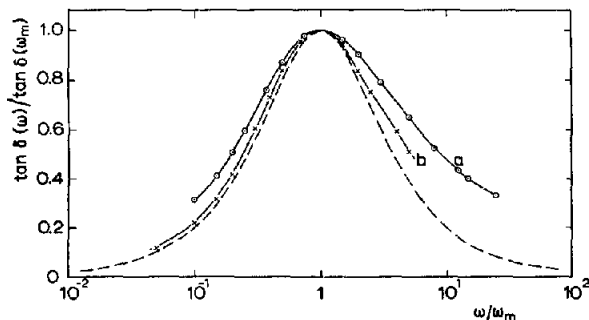


Fig. 1. Normalized $\tan \delta$ curves as a function of frequency at two temperatures.

	a	b
Temperature T	20.6°K	85°K
relaxation time τ	4×10^{-6} s	8×10^{-7} s
$\sqrt{\tau_H/\tau_L}$	2.85	1.7
$T \cdot \tan \delta(\omega_m)$	0.49	0.67

The dashed curve is the theoretical Debye curve.

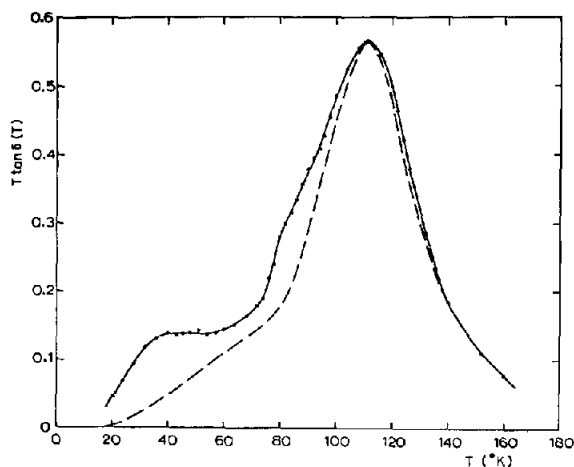


Fig. 2. $T \tan \delta$ curve as a function of temperature at 1 MHz. The humps at lower temperature are probably due to other (colour) centres. The dashed curve is the theoretical one, calculated with the help of the τ values from fig. 3.

shows $T \cdot \tan \delta$ versus temperature at a given frequency. In both graphs the theoretical curve is represented by dashes. It is evident from fig. 2 that two or more types of colour centres contribute to the dielectric losses in the temperature and frequency range investigated. Fortunately, in most cases it is easily possible to separate the dielectric losses due to the dominant type of colour centres from the contributions of the others. We confine ourselves here to the dominant type of centres. Another point is that the curves are somewhat flattened in comparison with the theoretical Debye curve, and

that the maximum value of $T \cdot \tan \delta$ is not constant over the whole temperature range. These aspects are dealt with in chapter V.

Fig. 3 shows $\log \tau$ as a function of $1000/T$ between 20 and 125°K. τ satisfies the formula:

$$\tau^{-1} = \tau_1^{-1} + \tau_2^{-1} \quad (2)$$

with $\tau_i = \tau_{0i} \exp(E_i/kT)$ $i = 1, 2$.

From the measurements given in fig. 3 we derive

$$\tau_{01} = (3.0 \pm 0.5) \times 10^{-7} \text{ s}; \quad E_1 = 8.5 \pm 0.5 \text{ meV.}$$

$$\tau_{02} = (2.5 \pm 1) \times 10^{-11} \text{ s}; \quad E_2 = 85 \pm 5 \text{ meV.}$$

At low temperature the results are comparable with the results of Stevels and Volger. At higher temperature, however, a second relaxation mechanism dominates by a much higher activation energy and a very much smaller pre-exponential factor.

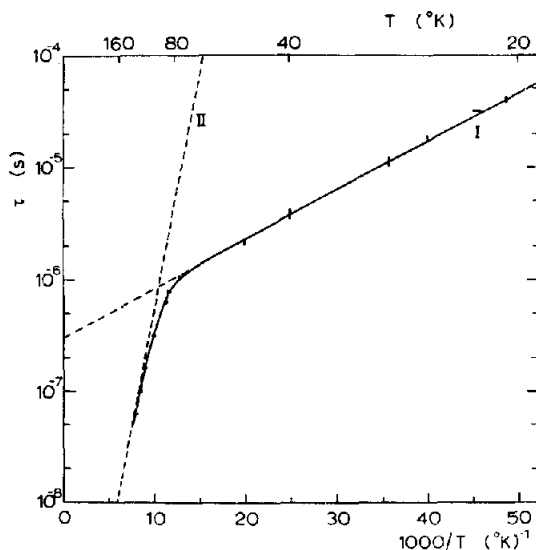


Fig. 3. The logarithm of the relaxation time τ as a function of $1000/T$.

Both relaxation mechanisms are due to the same type of colour centres. The activation energies are 8.5 meV and 85 meV, respectively, and the "tunnelling" relaxation times are 3×10^{-7} and 3×10^{-11} s.

Both mechanisms are due to colour centres, as was evidenced by the following observation: when the crystal is heated to 400 centigrade the colour disappears and the $\tan \delta$ of the colourless crystal becomes less than 10% of the $\tan \delta$ of the coloured crystal. When the crystal is recoloured by irradiation with X rays, the loss peaks reappear. It is also evident that both mechanisms are due to the same type of colour centres, for the ratio of the high temperature loss peak to the low temperature loss peak has always the

same order of magnitude, for different samples, with different impurity concentrations. With corrections for $\tan \delta(\omega_m)$ as mentioned in paragraph VI, we may even conclude to a ratio of about unity, so that the dipole strength must be about the same.

In section IV we will discuss a theory in order to explain the observed two relaxation mechanisms of one centre.

IV. *Discussions.* According to Sussmann*) a relaxation mechanism with a relaxation time depending exponentially on temperature can be explained with the help of transition states in the form of "non-localized states" even below the potential barrier in a double minimum potential well. These are good intermediate states for transitions of the particle from one side to the other, whereby the temperature dependence of the relaxation time τ is due to the fact that the particle must be thermally excited to one of these intermediate states. After having been tunnelled, through the barrier to the other side, it can finally fall back to the ground state, the ground state showing linear Stark effect since the "atomic" wave functions are supposed to be highly localized (little overlap). We shall take this model as adequate for the discussion of our experiments.

The inverse of the relaxation time is twice the excitation probability, multiplied by the fraction of particles, tunnelling through the barrier (in competition with those immediately falling back to the ground state):

$$1/\tau_i = 2[W_{0i} \cdot 2\omega_{ti} (2\omega_{ti} + W_{0i} \exp(E_i/kT))^{-1}]. \quad (3)$$

Here W_{0i} is the probability of excitation of the particle to a state i of energy H_i above the ground state by interactions of the phonons. ω_{ti} is the tunnelling or "resonance" frequency through the barrier:

$$\omega_{ti} = \Delta_i/\hbar, \quad (4)$$

where Δ_i is the energy difference between the symmetrical and antisymmetrical states of set i .

There are now two possibilities: The tunnelling probability of the particle is either very small or very large as compared with its chance to fall back to the ground state:

$$2\omega_{ti} \ll W_{0i} \exp(E_i/kT)$$

or

$$2\omega_{ti} \gg W_{0i} \exp(E_i/kT).$$

In the first case (small tunnelling probability) one obtains from eq. (3):

$$1/\tau_i = 4\omega_{ti} \exp(-E_i/kT)$$

or

$$\tau_i = \tau_{0i} \exp(E_i/kT). \quad (5)$$

*) The authors are indebted to Dr. J. A. Sussmann for sending them an early draft of his paper on "Tunneling of Ions as a Relaxation Mechanism in Solids".

Now Sussmann assumes that the inverse relaxation time is a sum of terms of the above form (see eq. 2), one for each set of symmetrical and anti-symmetrical states, plus of course a non-exponential contribution from phonon-induced tunnelling processes. The latter one may be dominant at much lower temperature, but this does not seem to apply to our measurements. The splitting Δ_i determines the pre-exponential factor in (5). For sets of states below the barrier this splitting may be very small, in fact several orders of magnitude smaller than they would be for sets above the barrier (see fig. 4). Consequently, for low-lying sets the pre-exponential factor

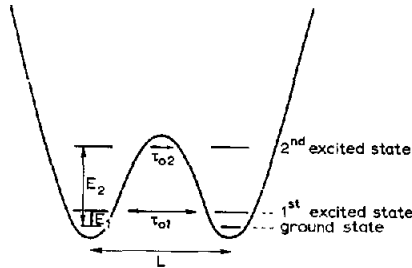


Fig. 4. Model of the one-dimensional double potential well. There are at least two sets of intermediate states, i.e. "spring-boards" for transitions through the potential barrier. The width of the potential barrier L can be estimated from the dipole strength:
 $L \approx 10^{-8}$ cm.

in expression (5) is very small, in fact much smaller than the classical oscillation frequency of the particle occurring when it is excited to sufficiently high-lying states in the potential well. Tunnelling transitions via low-lying states are therefore characterized by a remarkably large relaxation time, and of course a rather small activation energy.

In the second case (large tunnelling probability) no time delay in the transition or intermediate state is involved, and the excitation probability becomes the determining factor for the relaxation time. Since thermal excitation to the lowest intermediate state seems the most probable, we expect, in this second case, transitions mainly via the lowest state. From eq. (3) one obtains:

$$1/\tau = 1/\tau_1 = 2W_{01}.$$

Assuming that the experimental behaviour of the relaxation time in smoky quartz is to be explained with Sussmann's theory, as seems very likely, we conclude to at least two sets of intermediate states, i.e. "spring-boards" for transitions through the potential barrier. In other words, it is believed that two tunnelling processes, as described above, cause the temperature dependence of τ , observed by us and characterized by the parameters given in section III.

As mentioned in the introduction, Taylor and Farnell⁶⁾ found in

smoky quartz below 16°K another relaxation mechanism. There are now two possibilities to interpret those measurements:

- a) One can assume a third intermediate state, very close to the ground state (about 1 meV) and with a very small tunnelling frequency. Transitions via this state are then dominant between 4 and 10°K.
- b) But within the experimental accuracy it is also possible to conclude:

$$\tau = aT^{-x} \quad \text{with} \quad x = 1.5 \pm 0.25.$$

This is in agreement with the theory of phonon-induced tunnelling processes at very low temperature. Sussmann⁹⁾ obtains $\tau \sim T^{-1}$ for one-phonon processes and $\tau \sim T^{-2}$ for two-phonon processes. Other authors report on a similar behaviour of the dielectric relaxation time, e.g. in hydroxyl doped potassium chloride between 1.5 and 10°K¹⁰⁾. Our own preliminary measurements down to 4°K point into the direction of interpretation b).

V. *Discussions of the spread in the relaxation times.* a) Deviations from the Debye curve. From a comparison of the measured $\tan \delta$ curves in fig. 1 and fig. 2 with the theoretical Debye curve it appears that the experimental curves are always more flattened out than the theoretical one. It is known that this is caused by the existence of a distribution function $g(\tau)$, (which indicates how the relaxation times are distributed). With this distribution function $g(\tau)$ one obtains:

$$\frac{\varepsilon - \varepsilon_{\infty}}{\varepsilon_s - \varepsilon_{\infty}} = \int_0^{\infty} \frac{g(\tau)}{1 - j\omega\tau} d\tau.$$

A consequence of this distribution is also that the maximum value of $\tan \delta$ decreases with respect to the ideal Debye curve.

Fig. 1 shows that in our case the deviation decreases when the temperature increases. At higher temperatures the function $g(\tau)$ is approaching a δ -function: $\delta(\langle\tau\rangle - \tau)$ where $\langle\tau\rangle$ is the characteristic or central relaxation time. Obviously both relaxation mechanisms show also a different spread in relaxation times.

The experimental curves are never found to be narrower than the Debye curve, which indicates that in our temperature and frequency range only relaxation processes occur and no electronic resonance processes.

b) Determination of the distribution function $g(\tau)$. Fröhlich¹¹ assumed minimum and maximum relaxation times τ_L and τ_H and he used a distribution function of the form:

$$\begin{aligned} g(\tau) &= \left(\tau \cdot \ln \frac{\tau_H}{\tau_L} \right)^{-1} & \tau_L < \tau < \tau_H \\ g(\tau) &= 0 & \tau_H < \tau < \tau_L \end{aligned} \quad (6)$$

We shall work out Fröhlich's ideas in our analysis. The expression for $\tan \delta(\omega)$ now will be

$$\tan \delta(\omega) = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} \approx \frac{2\varepsilon''\omega}{\varepsilon_s + \varepsilon_\infty} = \frac{\varepsilon_s - \varepsilon_\infty}{\varepsilon_s + \varepsilon_\infty} \left[\frac{\tan^{-1} \omega\tau_H - \tan^{-1} \omega\tau_L}{\ln \sqrt{\tau_H/\tau_L}} \right]. \quad (7)$$

One obtains

$$\frac{\partial \tan \delta(\omega)}{\partial \omega} = 0 \quad \text{if} \quad \omega^{-1} = \omega_m^{-1} = \langle \tau \rangle = \sqrt{\tau_H \cdot \tau_L} \quad (8)$$

This leads with eq. (7) to the correction factor for $\tan \delta(\omega_m)$

$$G(\sqrt{\tau_H/\tau_L}) = \frac{\tan \delta(\omega_m)(\sqrt{\tau_H/\tau_L} = 1)}{\tan \delta(\omega_m)(\sqrt{\tau_H/\tau_L})} = \frac{\ln \sqrt{\tau_H/\tau_L}}{\tan^{-1} \sqrt{\tau_H/\tau_L} - \tan^{-1} \sqrt{\tau_L/\tau_H}}. \quad (9)$$

With the help of (8) and (9) expression (7) can be written in the form

$$\frac{\tan \delta(\omega)}{\tan \delta(\omega_m)} = \frac{\tan^{-1} \frac{\omega}{\omega_m} \sqrt{\tau_H/\tau_L} - \tan^{-1} \frac{\omega}{\omega_m} \sqrt{\tau_L/\tau_H}}{\tan^{-1} \sqrt{\tau_H/\tau_L} - \tan^{-1} \sqrt{\tau_L/\tau_H}}. \quad (10)$$

Defining now a ω_A such that $\tan \delta(\omega_A) = A \cdot \tan \delta(\omega_m)$ with $0 < A < 1$ and $\omega_A < \omega_m$, the above formula will be

$$\frac{\tan \delta(\omega_A)}{\tan \delta(\omega_m)} = A = \frac{\tan^{-1} \frac{\omega_A}{\omega_m} \sqrt{\tau_H/\tau_L} - \tan^{-1} \frac{\omega_A}{\omega_m} \sqrt{\tau_L/\tau_H}}{\tan^{-1} \sqrt{\tau_H/\tau_L} - \tan^{-1} \sqrt{\tau_L/\tau_H}}. \quad (11)$$

For the solution of (11) a graphical approach is followed. The results are given in fig. 5. Having derived ω_m/ω_A (for a chosen value of A) from the experimental $\tan \delta(\omega)$ curve (fig. 1), one now finds $\sqrt{\tau_H/\tau_L}$ directly from fig. 5. Since we also measure $\langle \tau \rangle = \sqrt{\tau_H \cdot \tau_L}$, we can calculate τ_H and τ_L separately in a simple way. The correction factor $G(\sqrt{\tau_H/\tau_L})$ (eq. (9)) for $\tan \delta(\omega_m)$ can be found from fig. 6.

The whole procedure can be repeated for different values of A . If the assumptions about the distribution function $g(\tau)$ are correct, the results will be independent of the choice of A . By this very simple method one is able to control the validity of the Fröhlich's distribution function $g(\tau)$, and, eventually, to determine the dispersion in the relaxation time and to calculate the correct value of $\tan \delta(\omega_m)$ in order to find the dipole strength. This method is simpler than that described by Mansingh and Kumar¹²), because this method can be used directly, for any substance, any temperature and any frequency.

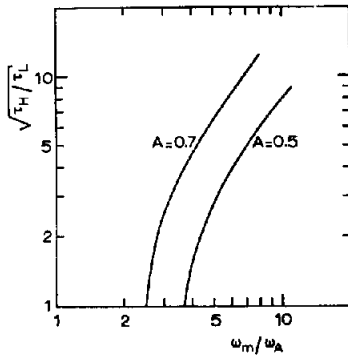


Fig. 5.

Fig. 5. The results of the graphical solution of eq. (11). For a chosen value of A one finds the spread in relaxation times $\sqrt{\tau_H/\tau_L}$ directly from the experimental value of ω_m/ω_A .

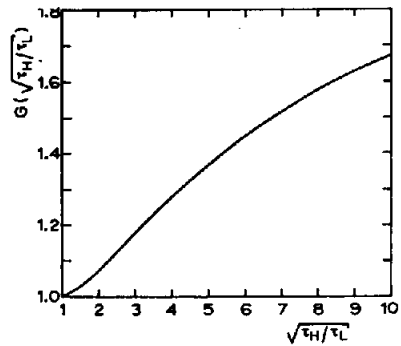


Fig. 6.

Fig. 6. The correction factor $G(\sqrt{\tau_H/\tau_L})$ for $\tan \delta(\omega_m)$ as a function of $\sqrt{\tau_H/\tau_L}$. See eq. (9)

c) The distribution of relaxation times in smoky quartz crystals. From a large number of $\tan \delta(\omega)$ measurements on smoky quartz – mostly at 20.5°K – different values for $\langle \tau \rangle$ have been found for different crystals. This is in agreement with the results of Stevels and Volger⁷⁾. Since no difference in activation energies was found – all the lines in fig. 3 for different crystals are parallel within the experimental error – we can write for τ_L and τ_H :

$$\tau_x = \tau_{0x} \exp(E/kT) \quad x = L, H \quad (12)$$

so that we obtain

$$\sqrt{\tau_H/\tau_L} = \sqrt{\tau_{0H}/\tau_{0L}} \quad (13)$$

and with help of eq. (8)

$$\langle \tau_0 \rangle = \sqrt{\tau_{0H} \cdot \tau_{0L}} \quad (14)$$

implying only a shift in the pre-exponential factor i.e. a shift in the tunnelling frequency.

In addition to the difference in the $\langle \tau \rangle$ values between the crystals there is also a difference in the dispersion of relaxation times $\sqrt{\tau_H/\tau_L}$. It appeared that the Fröhlich distribution function holds rather well indeed, since the same results for $\sqrt{\tau_H/\tau_L}$ were found for different values of the constant A in eq. (11).

In the low temperature region we find a connection between the position of the $\tan \delta$ peak along the frequency axis and the width of the $\tan \delta$ curve: the $\tan \delta$ curve is more flattened out, and thus ω_m/ω_A increases when the frequency ω_m increases. Using fig. 5 one finds, at low temperature, the relation between ω_m or $\langle \tau \rangle^{-1}$ and the spread in relaxation times $\sqrt{\tau_H/\tau_L}$. Now

from fig. 7 it is concluded that

$$\omega_m \propto \sqrt{\tau_H/\tau_L} \quad (15)$$

up to at least $\tau_H/\tau_L = 20$. With help of eq. (8), (13) and (14) we find

$$(\tau_{0H} \cdot \tau_{0L})^{-\frac{1}{2}} \propto (\tau_{0H}/\tau_{0L})^{\frac{1}{2}}$$

or

$$\tau_{0H} \text{ nearly constant.} \quad (16)$$

So we see that at low temperature the extreme value of the pre-exponential factor τ_{0H} is a constant for all the crystals. τ_H is the ideal relaxation time $\langle\tau\rangle$ in the case of no spread ($\sqrt{\tau_H/\tau_L} = 1$). If there is a spread in relaxation times a smaller mean value $\langle\tau\rangle$ is found.

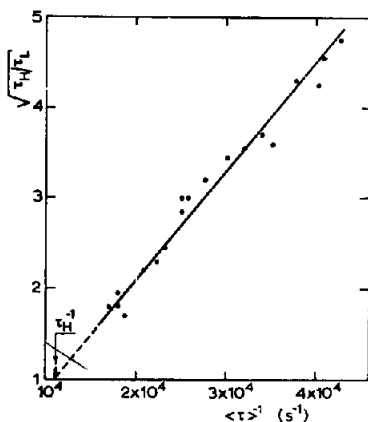


Fig. 7. The spread in relaxation times, $\sqrt{\tau_H/\tau_L}$, for various crystals as a function of $\langle\tau\rangle^{-1}$ at 20.6°K. Extrapolation to no spread ($(\sqrt{\tau_H/\tau_L} - 1)$) gives some idea about τ_H at this temperature. The corresponding τ_{0H} is about 10^{-6} s.

At higher temperature, however, above 80°K, we found for all the crystals only a very small spread and consequently about the same $\langle\tau\rangle$ values. Therefore, at high temperature the nearly ideal relaxation time is determined directly from the $\tan \delta$ curves.

Stevens and Volger⁷⁾ have suggested that the spread found in the $\langle\tau_0\rangle$ values is related to the spread in the bounding forces at the centres, and in particular to the stress fields due to an overall imperfection of the crystal. They found, for instance, increasing values for $\langle\tau_0\rangle$ with increasing contents of lithium as characteristic impurity. Also, crystals irradiated by neutrons showed high $\langle\tau_0\rangle$ values. Furthermore, those colour centres which persistently resist bleaching and are caught at the more effective moorings, give also rise to higher $\langle\tau_0\rangle$ values. The effect of all these local and long range defects on $\langle\tau_0\rangle$ must be a disturbance of the potential wells around the colour centres, since the relaxation times $\langle\tau_0\rangle$ depend strongly on the width

of the potential barrier in the double minimum potential well (see fig. 4). From our experiments, one must now assume that irregularities in the crystal, such as large dislocations, deep moorings and strong stress fields, produce a broad potential barrier, especially at the base of the barrier, and consequently a long relaxation time $\langle\tau_0\rangle$. However, the maximum value τ_{0H} is obviously limited, so that with increasing irregularities in the crystal the spread in relaxation times $(\sqrt{\tau_{0H}/\tau_{0L}})$ decreases.

VI. *The dipole strength of the colour centres.* Equation (1) will be in our case:

$$P^2 = 6.3 \times 10^{19} (T/N) \cdot \tan \delta_{\max}.$$

Here P is expressed in Debye units ($= 10^{-18}$ e.s.e.); N is the concentration of dipoles with moment P . Corrected $\tan \delta(\omega_m)$ should be used on account of the spread in relaxation times, according eq. (9) and fig. 6. For lithium doped crystals we find at 20.5°K:

$$P = 3.9 \text{ Debye units}$$

assuming colour-saturation, i.e. the concentration Li and Al impurities (each about $2 \times 10^{18} \text{ cm}^{-3}$) equals the concentration of dipoles. P increases with only 18% to about 4.6 Debye units at 80°K. From these very small variations of the dipole strength we may conclude that at low temperature as well as at higher temperature the main dielectric loss peak is due to the same dipoles. This conclusion has been used in the preceding chapters.

The dipole strength P leads us to the width of the potential barrier L :

$$L \approx 10^{-8} \text{ cm.}$$

The energy shift due to an external field of about 1000 V/cm will be:

$$\Delta e = 10^{-8} \times 10^3 = 10^{-5} \text{ eV.}$$

From $\langle\tau_{01}\rangle = 3 \times 10^{-7} \text{ s}$ and the relation discussed in chapter IV $\langle\tau_{01}\rangle = \hbar/4\Delta_1$, we find now for the energy splitting Δ_1 in the first excited state:

$$\Delta_1 \approx 5.10^{-10} \text{ eV.}$$

The energy splitting in the groundstate will even be smaller. Therefore, we may conclude to a linear Stark effect as mentioned in section IV.

VII. *Conclusions.* From our experiments we can now draw the following conclusions:

- 1) The dielectric behaviour of colour centres in smoky quartz shows between 20 and 160°K two relaxation mechanisms with different relaxation times and different activation energies.

- 2) Both mechanisms are due to the same type of dipoles. The dipole strength is about 4 Debye units.
- 3) The experimental behaviour can be discussed with the help of Sussmann's theory of intermediate states including tunnelling processes.
- 4) The experimental $\tan \delta$ curves are more flattened out than the theoretical Debye curve, especially at low temperature. Fröhlich's distribution function: $g(\tau) \propto 1/\tau$ for $\tau_L < \tau < \tau_H$ describes the deviations very well.
- 5) At low temperature different crystals show a different relaxation time $\langle \tau \rangle$, due to irregularities in the crystal. The activation energy, however, shows no spread. Consequently there is a spread in the pre-exponential factor $\langle \tau_0 \rangle$ between different crystals. At higher temperature no spread in $\langle \tau \rangle$ is found.
- 6) The $\tan \delta$ curves become narrower with increasing $\langle \tau_0 \rangle$, i.e. the spread in relaxation times, $\sqrt{\tau_{0H}/\tau_{0L}}$, decreases with increasing τ_0 . Moreover, it seems that τ_{0H} is a constant. For the relaxation mechanism at low temperature (20–80°K) $\tau_{0H} \approx 10^{-6}$ s.

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