FURTHER EXPERIMENTAL INVESTIGATIONS ON
THE DIELÉCTRIC LOSSES OF QUARTZ CRYSTALS
IN RELATION TO THEIR IMPERFECTIONS

by J. M. STEVELS and J. VOLGER

Summary
Low-temperature dielectric losses of crystalline quartz samples are studied and interpreted in terms of crystal imperfections and their possible deformations. The effect of aluminium and alkali ions (as impurities in the lattice) is determined. The dielectric behaviour of irradiated quartz samples is shown to be related to the presence of colour centres. The relaxation time involved is determined.

Résumé
Les pertes diélectriques à basse température des échantillons de quartz cristallin ont été étudiées et interprétées en liaison avec les imperfections et déformations possibles du cristal. L'influence des ions d'aluminium et d'alkali (considérés comme impuretés dans le réseau) a également été déterminée. Il apparaît que le comportement diélectrique des échantillons de quartz irradié est lié à la présence de centres de couleur. Le temps de relaxation correspondant a été précisé.

Zusammenfassung

1. Introduction

Since our earlier publication 1) on the subject mentioned in the title, a fairly large number of new experiments have been carried out, and it seems appropriate to give an account of the results.

In the latter publication we reported two new features of the dielectric behaviour of quartz crystals, viz. (a) Built-in chemical impurities may carry an electric dipole moment, giving rise to dielectric losses. These are governed by a relaxation time which in turn is determined by a small activation energy (of the order of 0.1 eV). (b) Colour centres in the quartz crystal, which may be produced by exposing the specimens to ionizing radiation, also make a marked contribution to dielectric losses, especially at low temperatures, since remarkably small activation energies (about 5 meV) are involved.

The losses mentioned under (a) have been named deformation losses. They were found first in silicate glasses 2) and afterwards in crystalline quartz. The
dipole orientation is probably a local process in which there are only relatively small displacements of the ions *).

The losses mentioned under (b) have been called colour-centre dipole losses 4). Their character has been discussed tentatively 5) as being due to electrons or holes trapped at various positions, between which electrically active transitions can occur.

The present investigation is an extension of the earlier work 1) especially as far as the variety and the treatment of the specimens are concerned. It has the following aims: (a) To offer a more profound or improved (chemical) identification of the various originators of the dielectric losses; (b) To gain more insight into the physical properties found.

Dielectric-loss measurements at low temperature are an interesting tool for the study of imperfections in solids 6). Quartz in particular seems to be a suitable substance for this type of investigation, for the following reasons: (1) Both natural and synthetic crystals are available containing a great variety of contaminations in various concentrations, giving rise to a wealth of phenomena. (2) Although the crystal is rigid, the interstices and channels in the structure permit the entrance (for instance by electrolysis) and exchange of interstitial foreign ions. (3) The hypothesis of associated and complex imperfections in quartz seems not to be very urgent so far. (4) Colour centres are readily obtainable and fairly stable at room temperature.

2. The measurements and the scheme of their interpretation

The losses are measured with the help of the bridge described earlier 7). Specimens have a thickness of about 1 mm and a surface area of about 1 cm². Electrodes are obtained by applying a colloidal silver paint. The temperature range explored is mostly 14 °K up to 150 °K. This can easily be achieved since the specimens are mounted inside a measuring cell which can be either insulated thermally from the bath (mostly liquid hydrogen) or brought into contact with the bath by introducing some gas. This gives rise to an improvement as compared with earlier work 1), viz. by making it possible to control the heat leak between measuring cell and bath, so as to achieve a stable temperature for each measuring point.

The temperature equilibrium within the measuring cell is assured by the permanent presence of some heat-exchange gas.

The treatment of the crystals will be discussed in the relevant sections.

*) The deformation losses have to be distinguished from the migration losses occurring at higher temperatures, where ionic displacements over larger (interionic) distances are possible 3). The migration losses also have a relaxational character, the difference being that the activation energies involved are much larger (of the order of 0.5 to 1 eV).
The results are mostly presented in the form of \( \tan \delta \) vs \( T \) curves, measured at a frequency of 32 kc/s. Our discussion will be based on the well-known relaxation formula

\[
\tan \delta = \frac{\Delta \varepsilon}{\varepsilon_\infty} \frac{\omega \tau}{1 + \omega^2 \tau^2},
\]

in which

\[
\tau = \tau_0 \exp (Q/kT)
\]

where \( Q \) is an activation energy and in which

\[
\Delta \varepsilon = \frac{4\pi f N p^2}{3kT},
\]

where \( N \) is the concentration of permanent dipoles with moment \( p \); \( f \) depends on the internal-field correction, and is \( \left( \frac{\varepsilon + 2}{3} \right)^2 \) assuming that the Lorentz field approximation holds. However, \( f \) would be approximately 1 if the internal electric field were to approach the outer electric field, especially if charge transport occurs between almost equivalent positions.

From the formulae (1), (2), (3) it is seen that \( N, p, \tau_0 \) and \( Q \) are the important quantities to be deduced from the experiments.

\( \tau_0 \) and \( Q \) can be obtained from loss measurements as a function of both frequency and temperature. Strictly speaking, a number of \( \tan \delta \) vs \( \omega \) curves should be measured at various temperatures, but for practical reasons we usually confine ourselves to the less elegant method of taking the \( \tan \delta \) vs \( T \) curves mentioned.

We now define \( T_m \) as the temperature where the \( \tan \delta \) vs \( T \) curve shows its maximum. Since

\[
\tan \delta \propto f(T) = \frac{1}{T} \frac{\omega \tau_0 \exp (Q/kT)}{1 + \omega^2 \tau^2 \exp (2Q/kT)},
\]

three cases should be considered.

Case (A), \( \omega \tau_0 \ll 1 \). In this case \( \tau_0 \) and \( Q \) can be obtained from \( T_m \) and its shift when the frequency is set at a different value \(^1\).

From eq. (4) it follows that

\[
kT_m = -\frac{Q}{\ln (\omega \tau_0)} \left\{ 1 - \frac{1}{(\ln \omega \tau_0)^2} + \ldots \right\}.
\]

We can also make use of \( T_{mc} \), the temperature where the \( T \) \( \tan \delta \) vs \( T \) curve shows its maximum. At \( T_{mc} \) the slope of the \( \tan \delta \) vs \( s \) curve is \(-\frac{\tan \delta}{T}\) (fig. 1).
Fig. 1. Overall picture of the positions of $T_m$ and $T_{me}$ in a tan$\delta$ vs $T$ curve taken at fixed frequency ($\angle \alpha = \angle \beta$).

Since

$$kT_{me} = -\frac{Q}{\ln (\omega T_0)},$$

a distinction can be made in the following way:

Case (Aa), in which $\omega T_0$ is small enough, so that $T_{me} \approx T_m$. This case is experimentally found when studying the deformation losses (secs 5 to 10).

Case (Ab), in which $\omega T_0$ approaches 1 and a noticeable difference exists between $T_{me}$ and $T_m$. This will be found when the colour centres are discussed (sec. 11).

Case (B), $\omega T_0 = 1$. Now

$$\tan \delta \propto f(T) = \frac{1}{T} \frac{1}{\exp (Q/kT) + \exp (-Q/kT)},$$

showing its maximum at

$$T_m \approx 0.8Q/k.$$  

Case (C), $\omega T_0 \gg 1$. Then

$$\tan \delta \propto f(T) = \frac{1}{T} \frac{1}{\omega T_0} \exp (-Q/kT),$$

showing its maximum at

$$T_m = Q/k \text{ (independent of } \omega).$$
DIELECTRIC LOSSES OF QUARTZ CRYSTALS

Figure 2 gives a quantitative survey of the different cases. Curve Aa shows a sharp maximum at a temperature \( T_m = T_{mc} \) that can be regarded as a measure of the activation energy, provided \( \tau_0 \) is known. In fact an energy scale indicating the \( Q \) values could be added to the temperature scale of the figures, with the aid of eq. (6). Curve Ab shows a less pronounced maximum, which however is again a measure of the activation energy, albeit that one should now either make use of eq. (5) or determine \( T_{mc} \) (cf. fig. 1) and use eq. (6).

The curves B and C can hardly be considered as reflexions of the Debije curves. They are entirely determined by \( 1/T \) (cf. eqs (7) and (9)) and the Boltzmann exponential and are almost flat over a large temperature region. Cases B and C have no bearing on the work described in this paper.

From the curves (in particular from the height of the peaks of curves of the types Aa or Ab) we can obtain \( Np^2 \). This means that \( p \) can be derived, provided that the concentration \( N \) of the centres is known, e.g. from chemical or spectrographical analysis, and on the other hand \( N \) may be deduced, once the value of \( p \) has been verified.

3. Relation between deformation losses, colour-centre dipole losses and extinction coefficient

In fig. 3 we present \( \tan\delta \) vs \( T \) curves for a synthetic quartz crystal, in fact the same specimen, C4 *), studied earlier 1). Curve 1 holds for the virgin crystal, curves 4, 5 and 2 hold for the same crystal, but with increasing colouration,

* This crystal was provided by Bell Telephone Laboratories, Murray Hill, N. J., U. S. A.
curve 4 being obtained by weak irradiation with electrons, curve 5 by electron irradiation in a dose of $10^7$ r, curve 2 by X-ray irradiation ($2 \cdot 10^6$ r), curve 3

Fig. 3. Tanδ vs $T$ curves for a synthetic quartz crystal, C4, measured at 32 kc/s. Part of the data in this figure can also be found in fig. 5 of an earlier paper 1). The insert shows the relation between the peak heights, at 18 and 38 °K respectively, which are supposed to be proportional to the concentration of colour centres and progenitors.
after bleaching. The numbers give the chronological order of the experiments. The virgin crystal (1) shows three peaks, viz. at 38, 60 and 95 °K. Apparently the 38° peak of the bleached crystal (3) is somewhat smaller than that of the virgin crystal. The peaks all disappear gradually upon irradiation, but at the same time a new peak, due to colour centres, appears at 18 °K. As is known from earlier work \(^1\) a broad hump also appears at about 70 °K. These will be analysed in secs 11 et seq.

The insert in fig. 3 shows the relation between the height of the peak at 38 °K (deformation loss) and the height of the peak at 18 °K (colour-centre dipole loss). It is seen that the relation is practically linear, as long as we compare curves 2, 3, 4 and 5, thus showing that the colour centres are formed at the cost of those original defects (progenitors) which cause the deformation losses. It seems, however, that a (small) part of the progenitors (difference between the curves 1 and 3) does not act in such a way that the original defect is found again after a subsequent irradiation and bleaching.

A similar case is given in fig. 4, representing the behaviour of a synthetic quartz crystal, C9, *) the difference compared with C4 being that here relatively large amounts of Al\(^{3+}\) and Na\(^+\) ions were deliberately built in (a quantitative analysis of the effect of the amount of chemical defects will be postponed to sec. 7).

*) This crystal was provided by G.E.C. Laboratories, Wembley, Great Britain.
Curve 1 is the curve for the virgin crystal, curve 2 is the one after X-ray irradiation (6.10^6 r), curve 3 after bleaching, curve 4 after a second X-ray irradiation (4.5.10^6 r). The numbers are given in the chronological order of the experiments.

The curves for C9 differ from those for C4 with respect to the following features:

1. The peak for the colour-centre dipole losses of C9 has a different character (relatively broader).
2. Its maximum is found at a different temperature (between 35 and 40 °K). This accounts for the peculiar form of the curves 2 and 4, since here the peak of the colour-centre dipole losses coincide — quite incidentally, as will be shown later — with the peak caused by the non-affected progenitors.
3. The X-ray dose used (which was sufficient to attack all progenitors in the case of crystal C4) was insufficient to make all original deformation losses disappear.

Again it can be concluded that colour centres are formed at the cost of progenitors, although it seems that in this case the conversion factor is smaller. Also, not all progenitors are restored by the bleaching process which makes the colour-centre dipole losses disappear.

As in the case of the curves for irradiated C4, a broad hump appears for irradiated C9 at about 70 °K.

Another interesting case is shown in fig. 5, representing the measured curves for a very dark natural smoky quartz (type Morion), C19, in different stages of bleaching *).

Curve 1 represents the original state, showing the typical features of colour-centre dipole losses. Here the low-temperature peak is found at 25 °K, and the usual broad hump at 70 °K is also present.

Upon bleaching to about 300 °C there is a gradual decrease after a few hours in the colour-centre dipole losses (curve 2). After prolonged bleaching at 300 °C curve 3 is obtained. A shift in the maximum of the curve along the T-axis can be observed: it lies now at about 35 to 40 °K.

In the case of curves 1, 2 and 3 the extinction of the sample was measured. The values of A given in table I were derived from the measured transmission D (in %) for light with a wavelength of 5500 Å and with the aid of the formula D = 92 e^{-A}, the factor 92 being approximately the transmission in per cent for a clear crystal corrected for the reflections. Since colour-centre dipole losses fall under case Ab of the previous section, Tm, Tme and Tme tanδ are also listed in table I. The latter quantity should be proportional to Np² (cf. eqs (1) and (3)).

*) This quartz crystal is of Ukrainian origin, provided by the Ukrainian Academy of Sciences, Kiev, U.S.S.R.
TABLE I

<table>
<thead>
<tr>
<th></th>
<th>D (%)</th>
<th>A</th>
<th>Tm (°K)</th>
<th>Tmc(°K)</th>
<th>Tmctanδ(°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>original crystal (curve 1)</td>
<td>43.5</td>
<td>0.74</td>
<td>25</td>
<td>40</td>
<td>56.10⁻²</td>
</tr>
<tr>
<td>after bleaching at 300 °C curve 2)</td>
<td>76</td>
<td>0.19</td>
<td>37</td>
<td>52</td>
<td>13.10⁻²</td>
</tr>
<tr>
<td>after prolonged bleaching at 300 °C (curve 3)</td>
<td>80.5</td>
<td>0.13</td>
<td>37</td>
<td>54</td>
<td>10.10⁻²</td>
</tr>
</tbody>
</table>

Fig. 5. Tanδ vs T curves for a natural smoky quartz crystal, C19, in different stages of bleaching. Measuring frequency 32 kc/s.

The proportionality between A and Tmctanδ is satisfactory, since A should be proportional to N.

Subsequent bleaching for a few hours at 400 °C yielded curve 4 (in the insert of fig. 5). Visually the crystal is now nearly colourless, but residual colour-centre dipole losses could be traced (with a maximum in the loss curve still at the same place). Also a new peak at about 60 °K appears. This newly formed deformation-loss peak must be due to a progenitor, differing from the main deformation-loss peak at 38 °K seen in figs 2 and 3.
The identification of this and other deformation losses will be treated in sec. 9. At this point, however, it may be remarked that the peak at 60 °K which, although small, is the dominant one in the deformation-loss curves of all natural clear specimens (cf. for instance fig. 7 in an earlier paper 1)) is due to a lattice imperfection in which lithium is involved. The conversion factor of the deformation loss towards the colour-centre dipole loss seems to be very large for the 60 °K peak, but the presence of progenitors, not showing up in the deformation loss, cannot be excluded.

Finally, curve 5 in the insert of fig. 5, was obtained after twenty hours bleaching at 550 °C. Surprisingly enough, the peak at 60 °K has almost disappeared, whereas a peak at 38 °K has come into existence. This is probably a spurious effect. Peaks at 38 °K practically always occur in the synthetic clear crystals, where we find them to be the dominant ones. We shall prove them to be due to lattice imperfections in which sodium is involved. Li⁺ ions can easily be exchanged for Na⁺ ions at these temperatures *), and it is felt that the source of Na⁺ ions found is a surface contamination possibly due to handling the crystal with the fingers. However, latent sources of an unknown nature in the bulk cannot be excluded.

4. The effect of irradiation by neutrons

Although the majority of our experiments relating to the effect of irradiation on crystals were performed with the aid of electrons or X-rays, a few were carried out with neutron fluxes.

The crystals were exposed to a neutron flux in a reactor with the normal energy distribution (that is to say, part of the neutrons having energies lower than 1 eV (slow neutrons), the other part having higher energies up to about 1 MeV (fast neutrons)).

Whereas the primary effect of X-ray or electron beams is ionization, the colour-centre formation being a secondary process involving electric-field induced ion transport, fast neutrons primarily cause direct knock-off processes by impact, in which case the above-mentioned ionization process also occurs.

In the latter case radiation damage (thermal spikes, local vitrification) of a rather serious character is found. A typical result is shown in fig. 6 9).

Curve 1 shows the deformation losses again of a clear synthetic crystal, C6. Curve 2 gives the loss after irradiation by a flux of $10^{18}$ fast neutrons per cm$^2$ **). The typical form of a colour-centre dipole-loss curve is obtained ($T_m = 32 ^\circ K$, $T_{me} = 45 ^\circ K$). Curve 3 is obtained after subsequent thermal bleaching at 300 °K for 5 hours. Now, the original curve is not restored; so the conclusion

*) Such experiments were carried out by Drs Haven and Kats of this laboratory and will be duly described elsewhere 8).

**) The irradiation by neutrons has been performed by the courtesy of the Reactor Centre Mol, Belgium.
Fig. 6. Effect of neutron irradiation on the dielectric loss of a synthetic quartz crystal, C6. Measuring frequency 32 kc/s.

is that those progenitors which give rise to deformation losses are not regenerated. It seems plausible that the locally vitrified regions act as a sink for certain mobilized ions, although a very small amount of the progenitors are seen to come back since low maxima of a few times $10^{-5}$ are visible in curve 3.

The effect of a very heavy dose of fast neutrons has also been studied. A natural quartz crystal, C 20, was exposed to a flux of $10^{20}$ neutrons per cm$^2$ and consequently coloured $\ast$).

Such a heavy dose is known to cause total vitrification (the specimen was considerably deformed). It is also known that irradiated glasses, although they may contain a large concentration of colour centres, do not exhibit colour-centre dipole losses $\ast$). In the vitrified crystal under consideration the same results were observed: the tan$\delta$ vs $T$ curve is a straight line, at a very low level, from 14 to 220 °K.

5. Anisotropy of deformation losses

Since $\alpha$-quartz is not a cubic but a trigonal crystal the dielectric constant is, in fact, a tensor. The anisotropy is known and not very pronounced. The ques-

$\ast$) This crystal was provided by Dr I. Simon of A.D.Little Inc., Cambridge, Mass., U.S.A.
tion arises, however, whether the contributions of the imperfections to the
dielectric properties show a greater anisotropy.

This question is of practical importance too, since it had been found that
a few specimens which did not exhibit deformation losses when clear, did yield
colour-centre dipole losses after irradiation. Samples that show neither type
of losses have also been encountered in our research. The cases first mentioned,
however, have puzzled us for a long time. They might be explained if the
deformation losses were highly anisotropic and the crystals, although containing
enough progenitors, had been cut in an unfavourable direction. It has been
proved that such an anisotropy exists indeed.

Table II gives some results on synthetic crystals *) from which samples
had been sawn in different directions. The angle $\theta$ between the $z$-axis and the
measuring electric field has been listed. The height of the peaks at $38$ and $95 \, ^\circ K$
in the $\tan \delta$ vs $T$ curves, measured at $32 \, k\text{c/s}$, is seen to be highly dependent on
the orientation.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$\theta$ (between $z$-axis and electr. field)</th>
<th>$\cos^2 \theta$</th>
<th>Peak height at $38 , ^\circ K$</th>
<th>Peak height at $95 , ^\circ K$</th>
<th>Field</th>
</tr>
</thead>
<tbody>
<tr>
<td>C11</td>
<td>$0^\circ$</td>
<td>1</td>
<td>$28.10^{-4}$</td>
<td>$2.0.10^{-4}$</td>
<td>$// z$-axis</td>
</tr>
<tr>
<td></td>
<td>$\approx 52^\circ$ (rhomb. face)</td>
<td>0.38</td>
<td>$9.5.10^{-4}$</td>
<td>$0.6.10^{-4}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$90^\circ$</td>
<td>0</td>
<td>$1.10^{-4}$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>C12</td>
<td>$0^\circ$</td>
<td>1</td>
<td>$20.10^{-4}$</td>
<td>$1.5.10^{-4}$</td>
<td>$// z$-axis</td>
</tr>
<tr>
<td></td>
<td>$\approx 52^\circ$ (rhomb. face)</td>
<td>0.38</td>
<td>$13.7.10^{-4}$</td>
<td>$1.2.10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>C17</td>
<td>$0^\circ$</td>
<td>1</td>
<td>$6.10^{-4}$</td>
<td>$-$</td>
<td>$// z$-axis</td>
</tr>
<tr>
<td></td>
<td>$90^\circ$</td>
<td>0</td>
<td>$0.2.10^{-4}$</td>
<td>$-$</td>
<td></td>
</tr>
</tbody>
</table>

The simplest model to account for this anisotropy is the one in which the
dipoles can be oriented along the plus or minus $z$-axis only. In this case only the
electric field component $E_z$ in the $z$-direction gives rise to polarization and after-
effects. $\tan \delta$ is a measure of the part of the field energy which is dissipated, so that

$$\tan \delta.E^2 = \tan \delta_z.E_z^2$$

and therefore

$$\tan \delta = \tan \delta_z.\cos^2 \theta,$$

*) Provided by Bell Telephone Laboratories, Murray Hill, N. J., U.S.A.
where \( \tan \delta_z \) is the loss factor when a field is applied in the \( z \)-direction. This relationship seems to be fairly well satisfied, especially by the data of crystal C11. The data of C12 fit worse, but one has to keep in mind that slight inhomogeneities of the impurity concentrations can occur. It should be added that sample C11 is known to contain some Ge which, when present in the solution, is reported to promote a better statistical distribution of impurities in the growing crystal.

A more general relation is

\[
\tan \delta_x E_x^2 + \tan \delta_y E_y^2 + \tan \delta_z E_z^2,
\]

and one could use this also, resulting in \( \tan \delta_x = \tan \delta_y = 0 \). However, the structure of the quartz crystal itself points in the direction of the simpler model. It has channels in the \( z \)-direction and in the directions of the \( a \)-axis, the first of which may, obviously also in the case of the deformation losses under consideration, act as a guide to ionic movements. This structure of \( a \)-quartz is more extensively discussed by Kats.

6. The relation between the peaks at 38 and 95 °K in the \( \tan \delta \) vs \( T \) curves

From table II in the preceding section it is seen that the peak heights at 38 and 95 °K, measured for C11 and C12, have an almost constant ratio. In so far as they showed these peaks, and within the limits of the measuring accuracy, this feature was observed with all crystals investigated.

In fig. 7 a plot is made of all relevant data. The straight line represents a
ratio of 10 between the peak heights. It is seen that the proportionality mentioned holds fairly well over a wide range of loss angles, in fact almost three decades. The provisional conclusion of this finding can be that the two relaxation effects seem to be very closely related: either there are two imperfections involved, occurring in a fixed concentration ratio, or there is one imperfection that manifests itself in two relaxation effects. We shall return to this question in sec. 10.

7. Discussion of measurements on a series of crystals, grown from source material with increasing amount of aluminium added

In fig. 8 a series of tanδ vs T curves is displayed, measured on synthetic crystals (C7 to C10) which were synthesized in a comparable manner by using the hydrothermal method with NaOH as a solvent *).

The most striking feature is the occurrence again of the pairs of peaks at 38 and 95 °K. It is the aim of this section to compare our results with what is known about the preparation of the sample. Upon request of the present authors the crystals were grown after adding known amounts of aluminium to the melting-quality quartz source material, which is normally used in the hydrothermal process. With amounts of aluminium added larger than 50 parts in 10⁴ by weight (relative to source material) the crystalline quality of the

*) These crystals were provided by G.E.C. Laboratories, Wembley, Great Britain, by courtesy of Dr L. A. Thomas.
synthetic deposit rapidly deteriorates so that specimens cannot be cut, and with 250 parts in $10^4$ no growth is obtained ***(.)

In table III the peak heights of the various crystals as given in fig. 8 are listed together with the known amount of aluminium added to the source material. The table also includes the ratios of the peak heights at 38 and 95 °K (which are also included in fig. 7). The tanδ peaks are found to increase monotonically with the amount of Al added to the source material.

In discussing these data a quantitative chemical analysis of the impurities actually built into the specimens would be very useful. Such an analysis, however, is very difficult, since very small quantities are involved and the detection of small quantities of sodium is complicated by a possible involuntary contamination during the process of analysis.

In the table two sets of concentration values are given, one originating from the makers of the crystals (the analysis not being made of the measured specimens, but of the mother crystals) and one originating from this laboratory (made of the measured specimens themselves).

In view of possible inhomogeneities and contaminations during the analysis (these being so important according to Mr H. Oortwijn and Mr J. Visser that they had to take elaborate precautions) we are inclined to believe that the values in the last column are particularly useful for quantitative comparison: it is striking that the increase by about a factor 15 for the peak heights both at 38 and 95 °K when passing from C8 to C9 is found again by the same increase in the sodium concentration found in this laboratory. On the other hand, it should be borne in mind that sodium could be taken up in the crystal in such a form as to cause no contribution to the dielectric-loss peak under discussion. At all events it seems that the sodium concentration in the crystals under discussion also increases monotonically with the aluminium concentration in the source material.

From the concentration analysis by the makers it may likewise be concluded that Na is built-in together with Al; the ratio of atomic concentrations in the crystal seems to be about 1:2 in many cases (the rest of the Al$^{3+}$ ions being probably accompanied by Li$^+$ or H$^+$ ions 8).

In view of the uncertainty in the determination of the various concentrations and a lack of further data, it is impossible to deduce quantitatively the relation existing between the concentrations of Al and Na in the source material, the solvent, and the crystal.

In concluding it should be mentioned that, upon irradiation the specimens C9 and C10 do not darken uniformly. They show a typical pattern, as is shown in fig. 9. This enlarged photograph shows the same pattern as has been reproduced in a letter to the editor by Thomas 12). The deterioration of the

***(.)Private communication of Dr L. A. Thomas.
TABLE III

<table>
<thead>
<tr>
<th>Al added to source material (parts in $10^4$ by weight)</th>
<th>peak height at $38^\circ K$ (32kc/s) $\times 10^4$</th>
<th>peak heights at $95^\circ K$ (32 kc) $\times 10^4$</th>
<th>ratio of peaks</th>
<th>concentration of Al in the mother crystal *) (ppm)</th>
<th>concentration of Na in the mother crystal **) (ppm)</th>
<th>concentration of Na in actual specimen ***) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7</td>
<td>5</td>
<td>3.8</td>
<td>0.3</td>
<td>13</td>
<td>67</td>
<td>45</td>
</tr>
<tr>
<td>C8</td>
<td>12.5</td>
<td>8.0</td>
<td>1.0</td>
<td>8</td>
<td>445</td>
<td>172</td>
</tr>
<tr>
<td>C9</td>
<td>25</td>
<td>135</td>
<td>15</td>
<td>9</td>
<td>670</td>
<td>365</td>
</tr>
<tr>
<td>C10</td>
<td>50</td>
<td>220</td>
<td>17</td>
<td>13</td>
<td>1100</td>
<td>390</td>
</tr>
</tbody>
</table>

*) The values were obtained by spectrochemical analysis in the G.E.C. Research Laboratories, Wembley, Great Britain. Not the actual specimen investigated by us, but another piece of the mother crystal was analysed.
**) Determined by flame photometrical methods in the G.E.C. Research Laboratories, Wembley, Great Britain. Same remark as under *).
***) Determined by flame photometrical methods by H. Oortwijn and J. Visser in this laboratory. The analysis was carried out on the same specimen as investigated by us.
crystal mentioned earlier in this section starts to make itself felt in these specimens. It is probable that tensions and many dislocations are formed, and this is of importance for the discussion in sec. 12.

8. Discussion of experiments with crystals subjected to ion exchange

It is generally accepted that the aluminium ions in quartz crystals take silicon sites. The lack of positive charge can be compensated for by the presence of interstitial alkali or hydrogen ions, which are available in the solution.

In earlier publications it was suggested that the peak at 38 °K is connected with the presence of hydrogen, since in a series of crystals it had appeared, fortuitously as we now know, that the infrared absorption band at 2·7 μ which doubtless is due to OH vibrations, and the height of the 38 °K peak varied monotonically under various conditions. However, apart from the evidence, given in sec. 7, that the 38 and 95°K peaks are both related to the presence of sodium, we present here a few experiments likewise giving some evidence in favour of the sodium hypothesis.

In the first type of experiment the role of hydrogen is taken over by deuterium. Measurements were first done on C24, a crystal grown in the usual way *), except that the water of the solvent was replaced by D₂O (the ratio of H to D in the solvent being 1/200). The tanδ vs T curve showed no deviation from its normal shape. In particular, the normal 38 °K peak was found again. In another experiment, a crystal, C10, was heated for 2 days at 1000 °C under a pressure of 25 atm of D₂O vapour. It is known that under these circumstances 8)13), hydrogen will be exchanged for deuterium, although such treatment may also affect mobile alkaline ions. The tanδ vs T curve of the treated specimen shows lower peaks but their positions are unaltered, and it seems also that no new peaks have been formed.

*) In Bell Telephone Laboratories, Murray Hill, N. J., U.S.A.
A second type of experiment was performed by means of electrolysis: In a crystal at least part of the alkali ions and protons were interchanged by a sweep experiment, i.e. the crystal cut perpendicular to the c-axis, was placed between electrodes, the anode being an alkali halide, so as to produce a stream of specific alkali ions into the crystal, and causing in particular the most mobile cations to disappear out of the crystal at the cathode. Fields of 10 to 1000 V/cm and a temperature of about 500 °C were applied.

Fig. 10. Sweep experiments with a natural quartz crystal, C29; tanδ vs T at 32 kc/s. (1) Virgin crystal; (2) after introducing Na⁺ ions; (3) after introducing K⁺ ions.

In fig. 10, curve 1 shows the tan δ vs T curve for a natural Brazilian quartz crystal, C29. This crystal had been irradiated, after which it showed the normal colour-centre dipole losses, and bleached again.

A sweep experiment as described above was now carried out, exchanging Li⁺ for Na⁺ ions, and the tanδ vs T curve taken. Curve 2 shows the results, suggesting that the two well-known peaks appearing at 38 and 95 °K are due to Na⁺ ions. As a check, Na⁺ ions were replaced by Li⁺ ions and a curve (not shown

*) Drs Haven and Kats carried out these sweep experiments.
in fig. 10) was found in which very small remnants of the peaks at 38 and 95 °K are seen and an indication is found for a small peak at 60 °K.

In a subsequent sweep experiment, K+ ions were introduced and the tanδ vs T curve taken. Curve 3 shows the result: remnants of the peaks at 38, 60 and 95 °K can still be seen, and a new large peak has come into existence at about 140 °K. It is reasonable to ascribe this latter peak to potassium.

In fig. 11 the results of another sweep experiment are shown, starting from a crystal, C25, containing about 3.10^18 Li+ ions per cm³, which is a relatively high concentration. Curve 1 shows the original tanδ vs T curve with a marked peak at 60 °K only. After having introduced Na+ ions by a sweep experiment, two peaks appear at 38 and 95 °K but the peak at 60 °K is considerably lowered (curve 2). After a new treatment in which Li+ ions are introduced, obviously at the cost of Na+ ions, the peak at 60 °K is markedly enlarged and only remnants of the peak at 38 °K, due to non-exchanged Na+ ions, are found (curve 3).

9. Identification of the peaks in the loss curves at 32 kc/s

As discussed in the foregoing sections, the quartz crystal may contain aluminium ions together with alkali ions or protons. With a view to identifying the various peaks in the loss curves, we shall restate in this section some earlier conclusions and summarize the experimental facts.

We will discuss the influence of the various alkali ions separately.

Lithium ions

It is believed that the 60 °K peak is due to the presence of lithium ions. There are two reasons for this statement:
(1) The sweep experiment mentioned in sec. 8 and illustrated by fig. 11.
(2) The fact that, although a small peak at 60 °K practically always occurs in natural and synthetic quartz crystals, a high peak is found in those cases (C25, for instance) where the chemically determined lithium concentrations are much larger than usual.

Sodium ions

It is believed that the 38° and 95 °K are both due to the presence of sodium ions:
(1) There is a striking proportionality between the peak heights at 38 and 95 °K (cf. sec. 6).
(2) There is a proportionality between the peak heights and the sodium concentrations (cf. table III).
(3) Swept-in Na⁺ ions give rise to the two peaks mentioned in a correct peak-height ratio, whereas subsequent sweeping-out makes these almost disappear.

Potassium ions

It is believed that the peak at about 140 °K is due to potassium ions:
(1) Apart from in amethyst, potassium has never been found by chemical analysis in natural quartz crystals, and normally the 140 °K peak is also absent. In synthetic crystals potassium has sometimes been traced but in a crystal, C22, especially grown in 1 N KOH as a solvent *), the 140 °K peak, if any, has a height less than 2.10⁻⁵
(2) However, with the help of a sweep experiment larger amounts of K⁺ ions can be introduced (sec. 8, fig. 11) giving rise to the mentioned peak in the tanδ vs T curve.

Rubidium ions

A crystal, C23, grown in 0·8 molar Rb₂CO₃ aqueous solution as a solvent, did not show any special new peaks. Apparently the Rb⁺ ion is too big to enter the crystal. However, the few sodium and lithium ions originating from contaminations of either the Rb₂CO₃ or the source material may find their way with relative ease into the growing crystal, since even in this case rather high sodium peaks (for instance 25.10⁻⁴ at 38 °K and 2.5.10⁻⁴ at 95 °K) and a lithium peak (2.10⁻⁴ at 60 °K) are observed in the tanδ vs T curve.

Other ions

Finally a few remarks will be made about other ions.

By a sweep experiment, similar to that described in sec. 8, it is possible to

*) This crystal was provided by Bell Telephone Laboratories, Murray Hill, N.J., U.S.A.
introduce Ag$^+$ ions. The tan$\delta$ vs $T$ curve is shown in fig. 12. It shows a new peak at 22 °K, which must be due to Ag$^+$ ions. It should be remarked that there is still left a small maximum at 38 °K. It was found that electrolysis carried out with the help of AgCl, which was not completely free of NaCl, resulted in a higher peak at 38 °K.

In a similar way Cu$^+$ ions may be introduced, resulting in a peak at 225 °K with a measuring frequency of 32 kc/s.

It is fairly probable that Fe$^{3+}$ ions, like Al$^{3+}$ ions, may take Si$^{4+}$ sites and will indeed be present in both natural and synthetic quartz crystals. We have undertaken no specific investigation into this matter. It may be suggested again 1) however, that the hitherto unidentified peak at 120 °K is correlated with Fe. Amethyst, which generally has a remarkably high iron concentration, may show a maximum of a few times $10^{-4}$ in the loss curve at that temperature.

Protons, which are present in many quartz crystals, since strong OH vibrations are detected spectroscopically 11), are now considered as not conclusively detected in the dielectric losses, in the frequency and temperature ranges discussed in this paper.
10. Determination of the dipole strength of the imperfections in clear crystals.
Discussion of a model of these imperfections

A determination of the dipole strength, \( p \), for an imperfection that is electrically active, is complicated by the fact that the concentration of the impurities causing such an imperfection cannot be accurately measured.

It becomes even more doubtful when the possibility is envisaged that part of the foreign ions are hidden, as it were, in electrically inactive imperfections. A third point of doubt is the internal-field correction as discussed in sec. 2.

Let us first discuss models of the imperfections in clear crystals.

With the help of these models we shall try to systematize in the variety of data, and in particular we shall discuss the loss phenomena connected with ions of the following series: \( \text{H}^+, \text{Li}^+, \text{Na}^+, \text{K}^+ \).

We know from the discussion in sec. 5 that ionic charges can move in the direction of the \( c \)-axis, that is, in the main channels of the crystals.

The models proposed are given in fig. 13 showing in a schematic way the various possible positions for the mobile ions, and also qualitatively the potential energy of the ion involved as a function of a coordinate \( x \) in the direction of the \( c \)-axis. It should be emphasized that the models are oversimplified and are only meant as tentative proposals, but the following facts speak in their favour.

If \( \text{H}^+ \) ions are present, it is known from the infrared work of Kats \(^{11} \) that these are very strongly bonded to the oxygen ions. Kats has arrived at two possible models: in the first one the hydrogen is found “ahead” of an oxygen ion adjacent to the \( \text{Al}^{3+} \) ion (fig. 13a); the second model placed the hydrogen ion between two oxygen ions belonging to a tetrahedron of which the \( \text{Al}^{3+} \) ion is the centre (fig. 13b). In both models the OH bond can show both stretching and bending vibrations. Since the OH bond is very strong, we assume that there is no transition of \( \text{H}^+ \) ions to another oxygen ion in the wall of the channel, at least so at the low temperatures investigated. This is in accordance with the evidence, given in sec. 8, that at low temperature no dielectric relaxation is coupled with the presence of centres in which \( \text{H}^+ \) ions are involved.

Figures 13c to e shows the models for the positions of the alkali ions in the channels. The potentials are sketched so as to accord with the experimental facts.

There is an overall potential well around the \( \text{Al}^{3+} \) ion of the order of 1 eV depth (this value determines roughly the diffusion and ionic conduction; cf. Verhoogen \(^{14} \)). Superposed on this overall potential are the series of relatively low barriers along the channel, due to binding forces, and the influence of ion size and steric hindrance. Disregarding possible states of higher energy at the flanks of the potential well, which are supposed not to be occupied, the situation at the bottom is chosen in such a way that in the \( \text{Li}^+ \) case (fig. 13c) only one kind of transition and therefore only the one relaxation process detected...
Fig. 13. Showing models of the positions of H\(^+\) and alkali ions in the channels of the quartz crystal, and the corresponding trends of the potential energy curves.

In our temperature interval shows up, whereas fig. 13d (the Na\(^+\) case) indicates two different kinds of transition and fig. 13e (the K\(^+\) case) one again. There is some continuity in this series of models. The known values of the activation energies involved (cf. also table VI) are used in figs 13c to e.

Let us now consider the Na\(^+\) case in more detail in order to calculate the
value of \( p \) related to the 38 °K peak in spite of the difficulties mentioned in the beginning of this section. Our most reliable analyses are given in table IV.

### TABLE IV

<table>
<thead>
<tr>
<th>Na/SiO(_2) (ppm)</th>
<th>( N ) (cm(^{-3}))</th>
<th>( (\tan \delta)_{\text{max}} )</th>
<th>( p ) (Debye units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8</td>
<td>18</td>
<td>4.8.10(^{17})</td>
<td>8.10(^{-4})</td>
</tr>
<tr>
<td>C12</td>
<td>60</td>
<td>1.6.10(^{18})</td>
<td>14.10(^{-4})</td>
</tr>
<tr>
<td>C9</td>
<td>272</td>
<td>7.2.10(^{18})</td>
<td>135.10(^{-4})</td>
</tr>
</tbody>
</table>

From eqs (1) and (3) and taking \( f = (\varepsilon + 2)^{\frac{2}{3}} \) with \( \varepsilon = 4.8 \) one finds

\[
p^2 = 6.3.10^{15} \frac{T}{N} \tan \delta_{\text{max}},
\]

where \( p \) is expressed in Debye units (= 10\(^{-18}\) e.s.e.). With this equation the fifth column of table IV is calculated. If the internal-field correction had been less drastic, the values of \( p \) would have been somewhat higher. The displacement of the ion is of the order of 1 Å.

As to the discussion of the 95 °K peak, \( p \) values are found which are about half the values for the 38 °K peak, since \( \tan \delta_{\text{max}} \) is a factor of 10 lower, but \( T \) a factor of 2.5 higher.

The model in fig. 13\( d \) is chosen in such a way that a Boltzmann distribution factor is not taken into account, although the necessity for such a procedure cannot be excluded.

A similar procedure for lithium, using the peak height at 60 °K, yields \( p \) values as given in table V.

### TABLE V

<table>
<thead>
<tr>
<th>Li/SiO(_2) (ppm)</th>
<th>( N ) (cm(^{-3}))</th>
<th>( (\tan \delta)_{\text{max}} )</th>
<th>( p ) (Debye units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5</td>
<td>103</td>
<td>2.7.10(^{18})</td>
<td>6.10(^{-5})</td>
</tr>
<tr>
<td>C25</td>
<td>113</td>
<td>3.10(^{18})</td>
<td>13.10(^{-5})</td>
</tr>
<tr>
<td>C0</td>
<td>189</td>
<td>5.10(^{18})</td>
<td>20.10(^{-5})</td>
</tr>
</tbody>
</table>

In view of the possible and obvious errors the only conclusion can be that the \( p \) values in this case are remarkably smaller; i.e. of the order of 0.3 to 0.4 Debye units.
Our earlier conclusion\(^1\), that dipoles of the order of 1 Debye unit are involved, seems to be established by this further analysis of the deformation losses in quartz crystal.

In conclusion, table VI gives a survey of the activation energies belonging to relaxation effects due to a few discussed centres (progenitors). These activation energies are calculated from the shift of the peaks in the \(\tan \delta \) vs \(T\) curves with frequency.

**Table VI**

<table>
<thead>
<tr>
<th>impurity symbol ( ^{15} )</th>
<th>peak temp. for 32 kc/s (°K)</th>
<th>( \tau_0 ) (sec)</th>
<th>( Q(\text{eV}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al}_P ) ( \text{Na} )</td>
<td>38</td>
<td>( 2.10^{-13} )</td>
<td>0.055</td>
</tr>
<tr>
<td>( \text{Al}_P ) ( \text{Li} )</td>
<td>95</td>
<td>( 2.10^{-13} )</td>
<td>0.14</td>
</tr>
<tr>
<td>( \text{Al}_P ) ( \text{K} )</td>
<td>60</td>
<td>( 2.10^{-13} )</td>
<td>0.089</td>
</tr>
<tr>
<td>( \text{Al}_P ) ( \text{K} )</td>
<td>140</td>
<td>( 2.10^{-13} )</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Fig. 14. \( \tan \delta \) vs \( T \) curves taken at three different frequencies on an X-irradiated synthetic crystal, C11. This crystal contains 0.02% Ge. See fig. 15.
11. The relaxation time connected with the low-temperature effect in irradiated material

It is the aim of this section to discuss somewhat more profoundly than has hitherto been done \(^1\) the relaxation governing the dielectric loss, due to colour-centre dipoles, and its temperature dependence in particular. Measurements on a synthetic X-irradiated crystal, C11, will mainly be used \(\ast\). Figure 14 gives \(\tan\delta\) vs \(T\) curves, taken at three different frequencies, from which \(T_m\) and \(T_{mc}\) of the colour-centre dipole-loss peaks can be deduced. Figure 15 gives an example of a \(\tan\delta\) vs \(\nu\) curve. It is seen that this curve deviates somewhat from the theoretical Debye curve, especially at higher frequencies; nevertheless it is felt that one relaxation time may be obtained from it. The various data are collected in table VII.

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{crystal C11} & \text{measuring frequency(kc/s)} & T_m \text{ (°K)} & T_{mc} \text{ (°K)} & (T.\tan\delta)_{\text{max}} & \tau \text{ (sec)} \\ 1000/T \text{ (°K\(^{-1}\))} \\
\hline
\text{data from } \tan\delta \text{ vs } T \text{ curves in } \text{fig. 14} & \text{100} & \text{45} & \text{70} & \text{6.10\(^{-6}\)} & \text{1.6.10\(^{-6}\)} & \text{14} \\text{vs } \nu \text{ curves} & \text{32} & \text{26} & \text{35} & \text{3.4.10\(^{-6}\)} & \text{5.0.10\(^{-6}\)} & \text{28} \\
\hline
\text{data from } \tan\delta & \text{5} & \text{18} & \text{20} & \text{3.2.10\(^{-5}\)} & \text{3.2.10\(^{-5}\)} & \text{50} \\
\hline
\end{array}
\]

\(*\) This crystal was provided by Bell Telephone Laboratories, Murray Hill, N. J., U.S.A.
In fig. 16 the relaxation time $\tau$ has been plotted logarithmically vs $1000/T$. In table VII the values of $(T\tan\delta)_{\text{max}}$ have been included. The constancy of this quantity is in agreement with eqs (1) and (3), the one exception at the top of the column probably being due to mixing of the high-temperature effect ("hump") with the low-temperature peak under consideration (cf. also sec. 13).

A straight line in fig. 16 appears, showing that the $\tau$ values obey eq. (2) quite well over a large temperature interval.

One finds in the case of C11

$$\tau_0 = 5.10^{-7} \text{ sec and } Q = 7.5 \text{ meV}.$$ 

For a crystal containing a very large amount of colour centres (C9, cf. fig. 4 or table III) we find a somewhat larger $\tau_0$ value, viz. $10.10^{-7} \text{ sec}$, but the same activation energy, as can also be seen in fig. 16.

It should be added that the various coloured crystals generally differ not only in the value of their dielectric loss, but also in the position of their $\tan\delta$ peaks along the $T$-axis. In connection with all data available this matter will be dwelt upon further in sec. 12, but here it may be remarked that, according to eq. (5) (case Ab), a slight change in $\tau_0$ might have a marked influence upon $T_m$ when $\tau_0$ approaches 1. With the measurements presented in this paper we
generally have $\omega = 2.10^5$, so that in this case a change of $\tau_0$ from e.g. $10^{-6}$ to $5.10^{-7}$ sec alters the scale for the $Q$ values along the $T$-axis by a substantial factor, viz. roughly 1.4. It seems, therefore, that with the measuring frequency used the exact position of the peaks along the $T$-axis is a rather sensitive measure of $\tau_0$, so long as one can be sure that cases with the same $Q$ value are compared. If we compare the cases of C9 and C11 (cf. fig. 16) having $T_{me}$ values of 50 and 35 $^\circ$K respectively (measured at 32 kc/s), a difference which may seem quite alarming at first sight, we have indeed a good example of this phenomenon, since these crystals have the same activation energy of the colour-centre dipole relaxation and differ in $\tau_0$ values by a factor of 2 only *).

A possible reason for shifts in $\tau_0$ will be discussed in sec 12. It seems likely that not only the local lattice disturbance at the point imperfection, but also long-range effects (tension in the crystal) are involved.

12. The spread in relaxational behaviour of various coloured crystals

In this section we shall deal mainly with the low-temperature effect of coloured crystals, i.e. the peak in the $\tan \delta$ vs $T$ curve at about 20 to 40 $^\circ$K. The high-temperature effect (hump at 70 $^\circ$K) will be discussed in sec. 13.

An important fact to be noticed is the spread of the $T_m$ and $T_{me}$ values in the numerous measured curves at our disposal. $T_m$ values are found ranging from 15 to 40 $^\circ$K. The reader is referred to the figures published earlier *) and figs 3, 4, 5 and 6 of this article, where a few examples are given. In view of the discussion in sec. 11, this spread should not worry us too much, since relatively small variations of $\tau_0$ already involve such large variations of $T_m$ and $T_{me}$.

Let us first discuss briefly what happens when the crystal is irradiated. The progenitors, discussed in the foregoing sections, are the spots where the ionizing radiation works. It causes dissociation of a progenitor into (1) an aluminium ion with a hole trapped at the neighbouring oxygen ions ($AlA^+$ centre) and (2) an alkali ion (X+) associated with a trapped electron ($XP^-$ centre). The latter centre must have found a relatively stable position at some mooring, most likely at an already existing irregularity, imperfection or impurity (foreign ion) in the lattice *).

On the basis of this picture we venture the hypothesis that the $XP^-$ centre gives rise to the main low-temperature loss peak, whereas the $AlA^+$ centre should be connected with the hump at about 70 $^\circ$K.

A similar hypothesis has been put forward earlier 1). At the time the spread of the $T_m$ values was interpreted in terms of the chemical nature of the alkali ions involved, but taking into account the now-available experimental evidence,

*) These complications are not encountered in the discussion of deformation losses, since $\tau_0$ is extremely small in that case (Aa).

*) Since the word “trap” has generally been accepted for the place where electrons or holes are captured, we prefer to speak of “moorings” for places where ions are captured.
we are inclined to believe that the influence of the said nature is small in relation to the influence of the nature of the moorings mentioned above. These moorings could be dislocations or in themselves rather inactive or harmless point defects, such as titanium or germanium on a silicon site, or an oxygen vacancy flanked by two substitutional aluminium ions.

Anderson and Weyl\(^{16}\) and Van Wieringen\(^{17}\) from e.p.r. and Kats\(^{18}\) from spectroscopic studies give evidence for the occurrence of colour centres, comprising a substitutional germanium ion, an interstitial sodium ion and an unpaired electron. Strictly speaking the electron could possibly first be trapped at the germanium, so as to form the mooring where subsequently the sodium ion is caught\(^{17}\). Substitutional germanium is known to lengthen the a-axis and to shorten the c-axis.

The spread in the relaxational behaviour (e.g. \(T_m\) values and \(\tau_0\) values), then, is related to the spread in bonding forces to the various moorings and to the stress fields due to the overall imperfection of the crystal.

We now shall give evidence for this point of view.

(1) Those natural clear crystals which are characterized by low concentrations of alkali impurities (and consequently by low deformation losses) and which, moreover, are grown very slowly, show low \(T_m\) values upon irradiation. This applies particularly to most of the smoky quartz crystals, being natural crystals irradiated in nature, in which low concentrations of impurities are found and in which \(T_m\) values below 14 \(^\circ\)K have been measured in all cases investigated by us\(^{1}\).

(2) Comparing natural clear crystals with increasing content of lithium as the characteristic impurity, that is, with increasing peak height at 60 \(^\circ\)K (at 32 kc/s), it is found that after irradiation these crystals show increasing \(T_m\) and \(T_{me}\) values, as appears from table VIII.

(3) A series similar to that discussed sub (2) is given in table IX, where the data for a number of synthetic crystals are collected. Here, the impurity content is measured by the peak height at 38 \(^\circ\)K (32 kc/s) since \(\text{Al}^3\) centres are the main progenitors.

It should be remarked that in the case of C23 a considerable lithium peak of at least \(10.10^{-5}\) is present, besides the sodium content corresponding to the given height of the 38 \(^\circ\)K peak.

(4) An interesting case is formed by the crystals irradiated by a flux of neutrons. Without exception such crystals (C6, C14, C17) show high \(T_m\) values (>30 \(^\circ\)K) and \(T_{me}\) values (>45 \(^\circ\)K). This will be due to irradiation damage, creating stress fields and an overall imperfection in the crystal as discussed above\(^{19}\).

We have done measurements on two specimens originating from the same mother crystal, one being irradiated by X-rays only (C6') showing a \(T_m\) value
TABLE VIII.

<table>
<thead>
<tr>
<th>crystal</th>
<th>peak height at 60 °K (measured ( \perp z )-axis, at 32 kc/s in the clear crystal)</th>
<th>( T_m ) of colour-centre dipole losses</th>
<th>( T_{mc} ) of colour-centre dipole losses</th>
</tr>
</thead>
<tbody>
<tr>
<td>smoky crystals mentioned sub (1)</td>
<td>unknown</td>
<td>&lt;14</td>
<td>&lt;16</td>
</tr>
<tr>
<td>C3</td>
<td>unknown</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>C2</td>
<td>1.7.10^{-5}</td>
<td>22</td>
<td>30</td>
</tr>
<tr>
<td>C28</td>
<td>5.10^{-5}</td>
<td>23</td>
<td>33</td>
</tr>
<tr>
<td>C25</td>
<td>13.10^{-5}</td>
<td>23</td>
<td>40</td>
</tr>
</tbody>
</table>

TABLE IX

<table>
<thead>
<tr>
<th>crystal</th>
<th>peak height at 38 °K (measured ( \perp z )-axis, at 32 kc/s in the clear crystal)</th>
<th>( T_m ) of colour-centre dipole losses</th>
<th>( T_{mc} ) of colour-centre dipole losses</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4</td>
<td>6.10^{-4}</td>
<td>18</td>
<td>24</td>
</tr>
<tr>
<td>C11</td>
<td>28.10^{-4}</td>
<td>26</td>
<td>35</td>
</tr>
<tr>
<td>C23</td>
<td>27.10^{-4}</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>C9</td>
<td>135.10^{-4}</td>
<td>38</td>
<td>50</td>
</tr>
</tbody>
</table>

of 25 °K, the other one by a flux of neutrons (C6) showing a \( T_m \) value of 32 °K.

(5) To conclude, mention should be made of our measurements displayed in fig. 5. The crystal under consideration, C19, although a natural smoky quartz, has a high impurity concentration viz. 5.10^{18} Li/cm^{3} and 5.10^{18} Al/cm^{3}. In its original condition (curve 1 of fig. 5) the \( T_m \) value is as high as 25 °K. In the last phases before total bleaching (curves 2, 3 and 4 of fig. 5) \( T_m \) becomes 35 °K (\( T_{mc} \approx 50 °K \). This means that those colour centres which persistently resist bleaching and are caught, obviously, at the more effective moorings, give rise to the higher \( T_m \) values.
13. Discussion of the high-temperature effect (hump) in the $\tan \delta$ vs. $T$ curves in irradiated material. General discussion of certain features of the colour centres

The hump occurring at about 70 °K in the $\tan \delta$ vs $T$ curves (32 k€/s) in irradiated material has been mentioned in secs 3, 11 and 12. We shall now discuss a few features of this hump.

For several of the crystals at our disposal, we plotted $T.\tan \delta$ vs $1/T$, so as to facilitate the separation of the effect from the one at lower temperatures, discussed already in the former sections. In such a graph both effects show symmetrical curves. The height of the high-temperature peak is generally about 50% of the one at the lower temperature. This suggests that both effects are bound up with the presence of the two colour centres $\text{Al}_{A+}$ and $\text{xP}_-$ (cf. sec. 12) originating from one progenitor.

Since the $\text{Al}_{A+}$ centre remains at the position of the progenitor and does not need the presence of a mooring, it is plausible that the hump invariably found at 70 °K is connected with this simple colour centre.

The low-temperature peak, as we have seen, may be found at various temperatures. In those cases where the low-temperature peak lies at the lowest temperatures (for instance, in natural smoky quartz crystals) the hump shows up very clearly (cf. figs 8 and 9 in an earlier paper 1)).

If the above hypothesis is correct, an insufficient number of moorings in the crystal would mean that the formed $\text{xP}_-$ centres are not stabilized, so that they must either recombine with $\text{Al}_{A+}$ centres or associate amongst themselves, e.g. forming clusters of X-atoms. Such clusters would have properties quite different from those of the single centres. Such a case might be expected in a crystal grown under conditions leading to a high degree of perfection. These conditions are believed to be fulfilled by z-growth on a basal cut seed plate. Such a case was indeed encountered in crystal C6', which only slowly darkened upon irradiation and for which the height of the high-temperature peak in the $T.\tan \delta$ vs $1/T$ curve is about four times the height of the low-temperature peak.

The reader is referred to sec. 4, where the effect of neutron irradiation is discussed. The specimen considered, C6, taken from the same mother crystal as C6' and therefore identical as far as the progenitors are concerned, does show both darkening and the low-temperature colour-centre dipole-loss peak (cf. fig. 6), the reason being that in our opinion the flux of neutrons has produced sufficient moorings.

The activation energy governing the high-temperature colour-centre loss effects can only be estimated to be of the order of 10 meV.

A more accurate determination of this quantity has not been attempted since the two relaxation effects are unfortunately too close together in the temperature and frequency ranges used.

As a closing remark it can be said that the electric dipoles of the colour centres, like the relaxation times involved, may depend on the nature of the alkali
ion involved, the nature of the moorings and the overall imperfection of the crystal. This follows from the fact that the conversion factor, deformation loss vs low-temperature colour-centre dipole loss, varies from case to case, the trend being that the colour-centre dipole strength of the more perfect crystals is larger. Values up to 4 Debije units may be estimated for NaP-centres, whereas for LiP-centres values of the order of 1 Debije unit are found. These values are somewhat lower than the provisional values mentioned earlier ²).

Although a rather specific model for the deformation losses in quartz has been offered with some confidence (in sec. 10), we feel rather reluctant to do so for the case of the colour-centre diple losses, albeit, as stated earlier, that we believe that in the latter case electronic rather than ionic transitions are involved ⁵)²⁰).

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