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OF THE
32nd ANNUAL SYMPOSIUM ON
FREQUENCY CONTROL

1978

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of the

THIRTY SECOND ANNUAL FREQUENCY CONTROL SYMPOSIUM

1978

Sponsored by



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THE CHARACTERIZATION OF SYNTHETIC QUARTZ BY USING INFRA-RED ABSORPTION

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Summary

Samples of quartz obtained over several years from 12 suppliers have been examined. Hydrogen is found to be the major impurity. Infra-red measurements show that there are linear relations between the absorption due to hydrogen at 3585, 3500, 3410, 3300 and 3200 cm^{-1} . A consideration of the intrinsic and practical problems of using each of these absorptions suggests that it is advantageous to use the absorption at 3410 cm^{-1} and a simple reciprocal relation between Q and the appropriately corrected extinction coefficient is suggested.

Measurements of infra-red Q at various positions in a crystal show that significant changes only occur in general due to changing the position of the measured sample in the Z direction. These changes become large as the average Q falls. Similarly comparing the mean Q's of crystals from one batch shows that deviations from the batch mean increase as the batch mean falls. It is also shown that there is an inverse correlation between dislocation density and Q.

Introduction

The electromechanical Q of a quartz crystal is a useful guide to its suitability for various applications. Because high Q material must be grown slowly¹⁻⁴, it is expensive and should not be used unnecessarily. Direct measurements of Q are difficult to make. Thus a simple indirect method of measurement is needed. Dodd and Fraser⁵ showed that there is a good correlation between electromechanical Q and infra-red absorption and this method is now used by most workers in the field. Sawyer⁶ showed that the relation took the form

$$Q^{-1} = Q_0^{-1} + A\alpha + B\alpha^2 \quad (1)$$

where α is the extinction coefficient. Strictly, α is defined so that the fractional intensity of light transmitted through a parallel sided sample of thickness t is

$$T = \frac{(1 - R)^2 10^{-\alpha t}}{1 - R^2 10^{-2\alpha t}} \quad (2)$$

where R is the reflection coefficient of the sample surfaces and the denominator allows for the

effect of multiple internal reflections. For quartz in the near infra-red, R is about 4% so that the term $R^2 10^{-2\alpha t}$ has a maximum value of less than 2×10^{-3} and can be neglected. However a reliable estimate of α still requires measurements to be made on samples with different thicknesses. This was done by Lias et al² but other workers⁶⁻¹⁰ compare measurements at two wave numbers, one of which is chosen to have negligible absorption but essentially the same reflection coefficient as the frequency of interest. Then

$$\alpha = [\log_{10} (T_{\text{ref}}/T_v)] / t \quad (3)$$

where T_{ref} is the transmitted intensity at the reference wave number (usually 3800 or 3900 cm^{-1}) and T_v is the transmission at the wavenumber of interest. Table 1 summarizes the data in the literature in terms of coefficients in equation (1). Lias et al³ give data which relates α and hydroxyl content. At 3500 cm^{-1} they find that $\alpha = 1 \text{ cm}^{-1}$ corresponds to 4800 ppm H measured relative to silicon. Sawyer⁶ suggests a figure of 6000 ppm (cm^{-1})⁻¹.

This paper compares results obtained at the various wavenumbers sensitive to the presence of OH and shows that there are significant effects due to finite absorption independent of the hydroxyl content and that apparatus parameters (resolving power and polarization) can appreciably alter the results obtained. From the results obtained it is also shown that the variations of Q within a crystal and between crystals in a batch both increase as Q falls and that there seems to be an inverse correlation between Q and dislocation density.

Experimental

Samples were cut from crystals with Y-bar or Y-plate seeds obtained over a six year period from 12 suppliers (3 in the USA, 4 in Europe, 2 in Japan and one each in Russia, China and South America). From each supplier we obtained as many grades of material as possible. Thus the samples should be a representative selection of materials grown from various raw materials with a reasonable range of growth parameters. Table 2 gives the impurity contents found and shows that hydrogen is always the major impurity on an atomic basis. The only other significant trends observed were that high Q crystals tended to have less of all the impurities than low Q crystals (the upper quartile

data are typical of crystals with a Q of about 1×10^6 and the lower quartile figures are typical of samples with a Q of 2×10^6). Note also the effect of mineralizer on carbon content.

The samples for infra-red measurements were usually plates with faces including the X and Z axes and the radiation was propagated parallel to Y. The samples were polished usually finishing with Syton but for some samples we used cerirouge. If these samples were repolished on Syton, no significant differences were seen optically but double crystal reflection topographs showed that the cerirouge finish left some surface strains.

The measurements were made at room temperature ($20 \pm 5^\circ\text{C}$) generally using a Perkin-Elmer 337 double beam spectrometer. The beam size was stopped down to 5mm diameter. Because of the use of a reflecting optical system the radiation was polarized so that about 70% of the electric vector lay in a horizontal plane. We measured the crystals with the optic axis horizontal and vertical and deduced values of respectively α_{11} and α_1 as discussed later. The symbol α is used to imply the mean of these measurements. Similarly T implies the mean of the two transmitted intensities. Comparing our results with those obtained on the same samples with 3 other spectrometers showed that in general the T values agreed to within $\pm 0.5\%$ and results were reproducible to about 0.2%. Thus we believe that our measurements of the product αt (equation 3) are accurate to ± 0.005 , i.e. for a 10mm thick sample we can measure α to $\pm 0.005 \text{ cm}^{-1}$. The only exception to this was the measurement of α_{3585} . For this parameter we found that the resolving power of the instrument was important. Other spectrometers with resolving powers of about 4 cm^{-1} like ours gave the same result but instruments with better resolving power ($< 1.5 \text{ cm}^{-1}$) gave values which were higher by 15% on average. Thus for this line instrument resolving power is important. Other workers find the same effect. Thus due to a change in resolving power the calibration curves given in references 9 and 10 differ by a factor 2.

We measured plates between 1 and 20 mm thick but discarded results on plates less than 7 mm thick except for measurements of absolute absorption. We also discarded measurements on crystals which reflection topographs showed to be highly strained. These crystals could have values of $\alpha_{11}:\alpha_1$ which were radically different from the average e.g. 2.

Attention was concentrated on the Z growth zone and only these results are discussed in the next section. Values of α in the +X zone were usually larger than in the Z zone. This would be expected from the greater segregation coefficients (see reference 11 for a discussion of this).

Results and Discussion

Figure 1 shows the general features of the transmission spectrum of a typical sample. The two curves are for the same area but the upper

curve is T_1 and the lower curve is T_{11} . Kats¹² observed a similar sensitivity to polarization. His results taken at a temperature of 78K with 100% polarization show larger ratios than our data for about 300K with 70% polarization, see Table 3, which indicates that polarization effects can be significant.

Most workers use absorption at 3500 cm^{-1} as a measure of the quality of the crystals. Kats¹² has shown that much of the absorption in the near infra-red is due to hydrogen. Thus the lines at 3517, 3510 and 3485 are associated with hydrogen alone and the lines at 3513, 3510 and 3500 are associated with hydrogen and Na, Li and Ag respectively. Figure 1 shows that the absorption changes rapidly with wavenumber in this region. Typically a 1 cm^{-1} change in wave number changes α by 1%. Few spectrometers are reproducibly accurate to more than a few cm^{-1} so that errors of a few per cent can occur from using this absorption. A self locating line is therefore desirable but as was shown in the last section the line at 3585 cm^{-1} is so narrow that the result obtained depends to a large extent on the instrument resolving power. Kats¹² shows that this line is associated with H alone or H + K. The absorptions at 3410, 3300 and 3200 cm^{-1} are similarly associated with hydrogen with possible components due to hydrogen plus Na, Ag, Li and Cu. Kats¹² shows that there are lattice absorptions at 3396, 3300, 3220 and 3204 cm^{-1} and the half widths of these absorptions are typically 20 cm^{-1} so that a combined H and lattice effect is likely to be seen. However the lines at 3410, 3300 and 3200 cm^{-1} are easily located and the line at 3410 is very broad and therefore easy to locate and measure with any spectrometer.

Figure 2 gives data comparing α_{3410} with α_{3500} which from the published data^{2, 13} seems to be linearly proportional to hydroxyl content. (The value of α_{3585} is similarly linearly related to hydroxyl content¹³). The average data spread on Figure 2 is $\pm 7\%$ about the line

$$\alpha_{3410} = 0.050 + 1.25\alpha_{3500} \quad (4).$$

This data spread is expected on the basis of experimental errors. Similarly we find that with spreads of $\pm 8\%$ the other relative extinction coefficients (equation 3) can be given by

$$\alpha_{3300} = 0.125 + 0.80\alpha_{3500} \quad (5)$$

and

$$\alpha_{3200} = 0.110 + 0.60\alpha_{3500} \quad (6).$$

Our measurements of $\alpha_{3585}:\alpha_{3500}$ show that the average value is 1.03 ± 0.08 . It is possible that the ratio is slightly dependent on α . We find a ratio of 0.97 ± 0.05 for $\alpha < 0.1 \text{ cm}^{-1}$ and 1.07 ± 0.05 for $\alpha > 0.1 \text{ cm}^{-1}$. These differences are probably due to the resolving power effect already discussed. The uncertainties quoted in all these instances are spreads of the data points. Uncertainties in the mean values are much less.

In general our data show that for unstrained

samples there is little variation in the transmission of any sample in the range 4000 to 3760 cm^{-1} . (Badly strained samples show reproducible variations in this range.) However we did observe that the values of T varied with thickness from about 83 to 94%. Figure 3 plots the average values as a function of sample thickness. The slope of the line on this figure suggests an intrinsic extinction coefficient of $0.025 \pm 0.002 \text{ cm}^{-1}$ in this range. Kats¹² suggests that there may be lattice absorptions. If this is the case then the relative extinction coefficients (equation 3) will be smaller than the absolute ones (equation 2) and to convert from relative to absolute we must add 0.025 cm^{-1} . If this is done, equations (4) to (6) become

$$\alpha_{3410} = 0.044 + 1.25\alpha_{3500} \quad (7)$$

$$\alpha_{3300} = 0.130 + 0.80\alpha_{3500} \quad (8)$$

$$\text{and } \alpha_{3200} = 0.120 + 0.60\alpha_{3500} \quad (9)$$

Thus the intrinsic lattice absorptions at these frequencies correspond to absolute extinction coefficients of 0.044, 0.120 and 0.110 cm^{-1} . To obtain the hydroxyl related extinction coefficient from a relative one we must allow both for these absorptions and the intrinsic absorption at the reference frequency. Thus we add 0.025 cm^{-1} at 3500 and 3585 cm^{-1} and subtract 0.019, 0.105 and 0.095 cm^{-1} at 3410, 3300 and 3200 cm^{-1} respectively. Values treated in this way are denoted by α^* .

Figure 4 shows a plot of Q against α^* using the published data. It can be seen that for 3500 cm^{-1} the data are well represented by

$$Q = C \times 10^5 / \alpha_{3500}^* \quad (10)$$

where $C = 1.35$. The spread is that expected from experimental errors. The Toyo data for 3585 cm^{-1} seem to be well represented by the same equation but from our measurements we expect $C_{3585} = 1.39$ or for a spectrometer with a resolving power of better than 1.5 cm^{-1} , C_{3585} should be 1.60. Similarly at the other wavenumbers we can derive values of C from equations (7) to (9) which are $C_{3410} = 1.69$, $C_{3300} = 1.08$ and $C_{3200} = 0.81$. In practice only the absorption at 3410 cm^{-1} offers any appreciable advantage and we recommend the use of this line and the relation

$$= 1.69 \times 10^5 / \alpha_{3410}^* \quad (11)$$

There seems little doubt that a relation like (10) or (11) can be used with at least the same degree of confidence as any of the relations given in Table 1.

Now that we have a measurement technique, there is still a sampling problem: one measurement of Q does not characterize a crystal and measurements on one crystal do not characterize a batch grown in the same autoclave at the same time. Looking first at the variations in one crystal, we find that moving the beam in the X direction does not change α significantly unless there is a sub-

boundary (Figure 5) and such regions give large polarization effects: $\alpha_{11}:\alpha_1$ ratios of 1.5 or even 2. Similarly, if we measure another slice from the same crystal and make our measurement at the same distance from the seed, the changes are barely significant 15% for a Q of 1.0×10^6 , 10% for a Q of 1.5×10^6 and perhaps 5% for a Q of 2.5×10^6 . However when the beam is moved parallel to the Z axis large changes occur. Figure 6 shows the average change $\Delta\alpha^*$ obtained by moving a 5mm diameter beam in the Z direction by 5mm. The value of α decreases by an amount $\Delta\alpha^*$ on moving outwards. The figure gives the mean value of $\Delta\alpha^*$ as a function of the average of the two measured values of α^* . For most purposes the values of $\Delta\alpha^*$ and α^* probably characterize the crystal adequately. If we now examine the variations within a batch of Q deduced from α^* we find the relation shown on Figure 7. The values obtained for batches with the same mean Q are surprisingly constant. The standard error of the standard deviation is only about 20%. Thus we can use Figure 7 to deduce confidence limits based on measurements of a relatively small sample of crystals from one batch.

Because we had topographs of samples from crystals with known Q we could correlate dislocation densities with Q as shown on Figure 8. On this figure, open circles are median values and the filled circles and triangles represent respectively the maximum and minimum values found in batches of 8 to 12 samples. Thus it appears that a Q specification also fixes the likely range of dislocation densities. A relation between dislocation density and Q or α is reasonable on the model proposed by Griggs¹⁴ who suggests that dislocations are surrounded by a cloud of hydroxyl ions and Ayensu and Ashbee¹⁵ have proposed that dislocation movement requires OH ions. (Dislocation generation requires dislocation movement.)

Conclusions

This paper has shown that infra-red measurements can be used to characterize quartz. In order to obtain reasonable accuracy a relatively thick sample must be examined: for measurement of high Q 's a sample 10mm or more thick must be used. Account must be taken of polarization effects and intrinsic absorptions but if these are treated correctly a simple reciprocal relation gives Q . It is specifically recommended that when comparable results are required from different instruments the absorption at 3410 cm^{-1} should be used. Absorption at this wave number has the following advantages:

- It shows the maximum sensitivity to hydroxyl concentration.
- The line is easily located.
- The line is broad so that no problems are experienced with resolution or instrument calibration.
- The correction needed to convert relative extinction to absolute extinction due to hydroxyl is the smallest of any line considered.

(e) The polarization effect is small.

It is also necessary to measure at more than one location relative to the seed. If all these factors are taken into account then a batch can be characterized by measurements on a relatively few specimens. The polarization effect can be used to detect strained crystals and it appears that a measurement of Q fixes the range of dislocation densities likely to be found.

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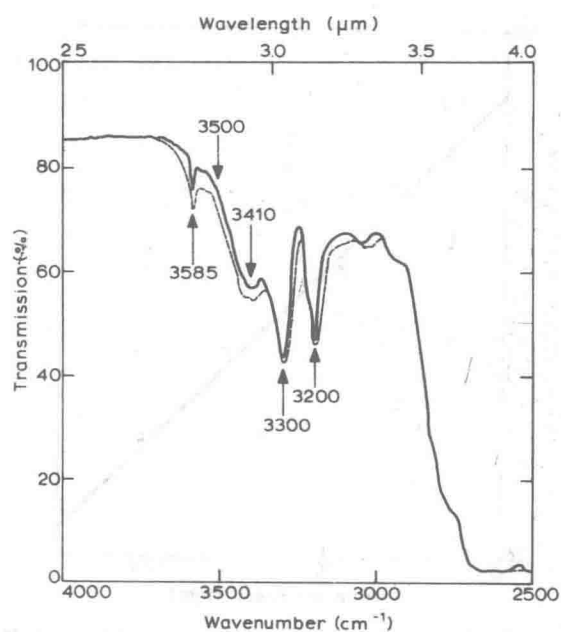


Figure 1. The transmission spectrum of a 20mm thick sample. The full line is obtained when the major part of the electric vector is parallel to Z. The broken line is the result obtained with the sample rotated 90° about Y.

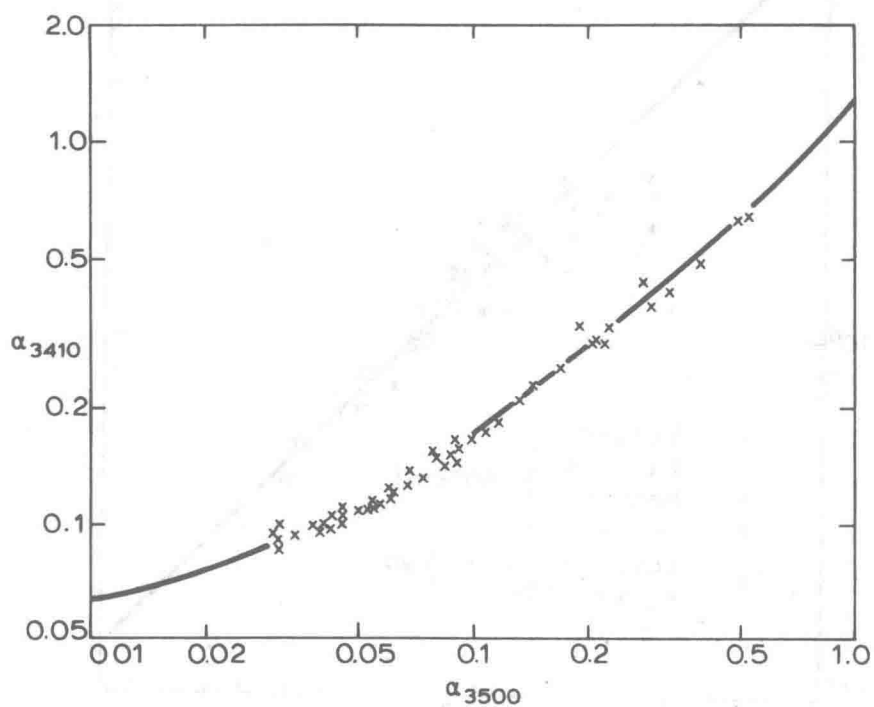


Figure 2. The comparison of α_{3410} with α_{3500} .

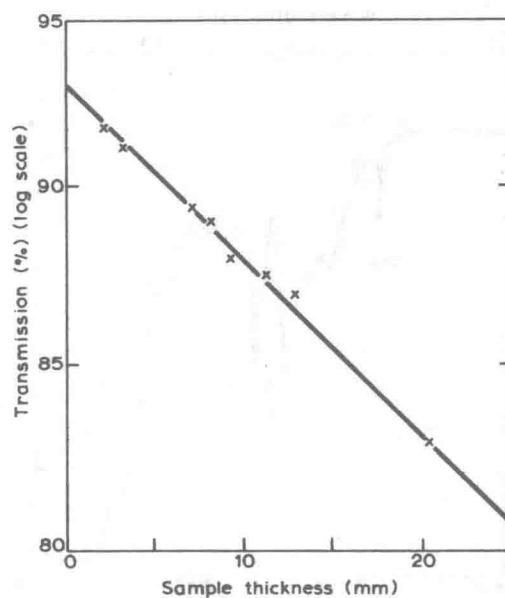


Figure 3. Average transmission in the range 3800 to 3900 cm^{-1} as a function of sample thickness.

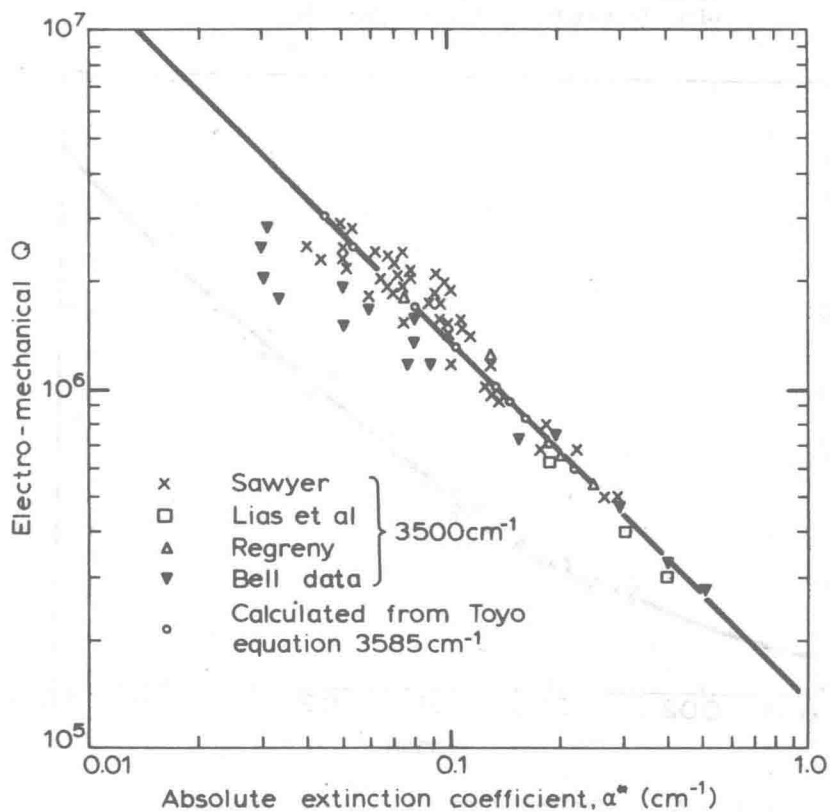


Figure 4. Published data on Q plotted as a function of α^* .

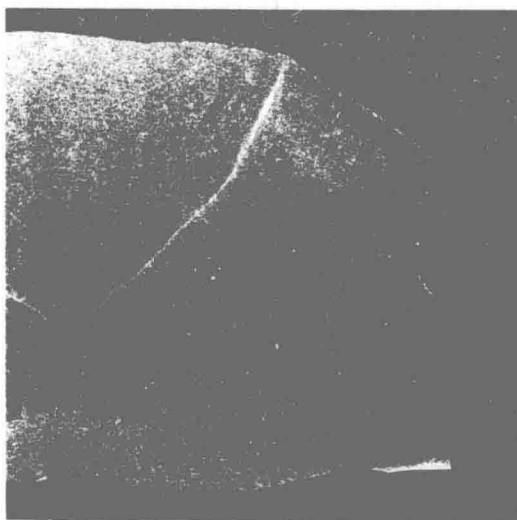


Figure 5. A double reflection X-ray topograph showing a "sub-boundary" in the Z zone.

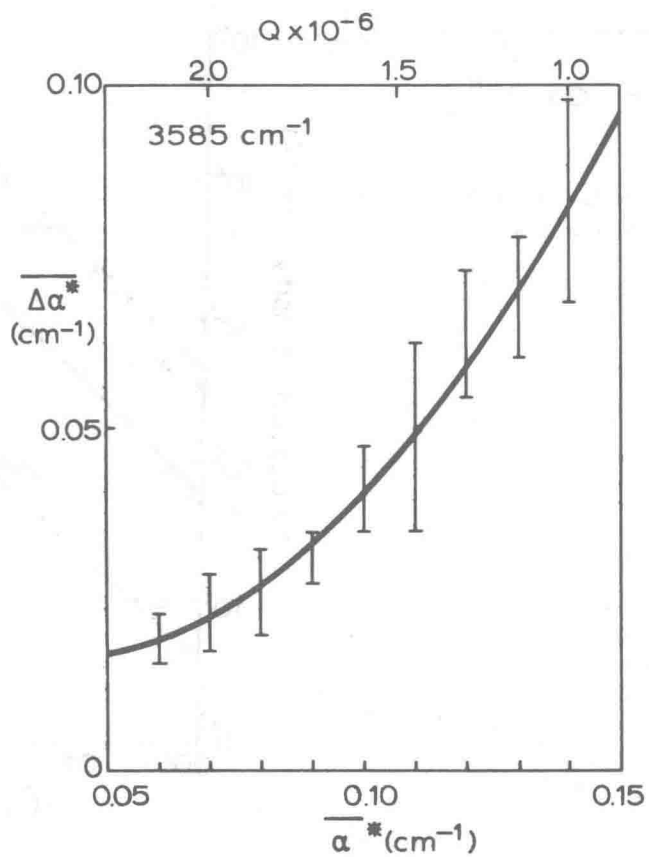


Figure 6. The change in α^* found on moving 5mm in the Z direction as a function of the mean value of α^* .

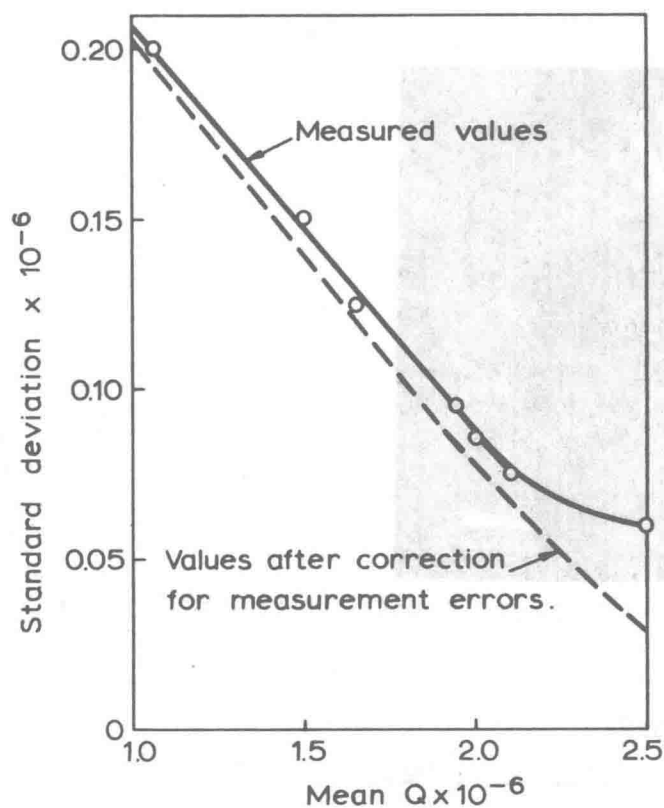


Figure 7. The standard deviation of Q in batches with different mean Q 's.

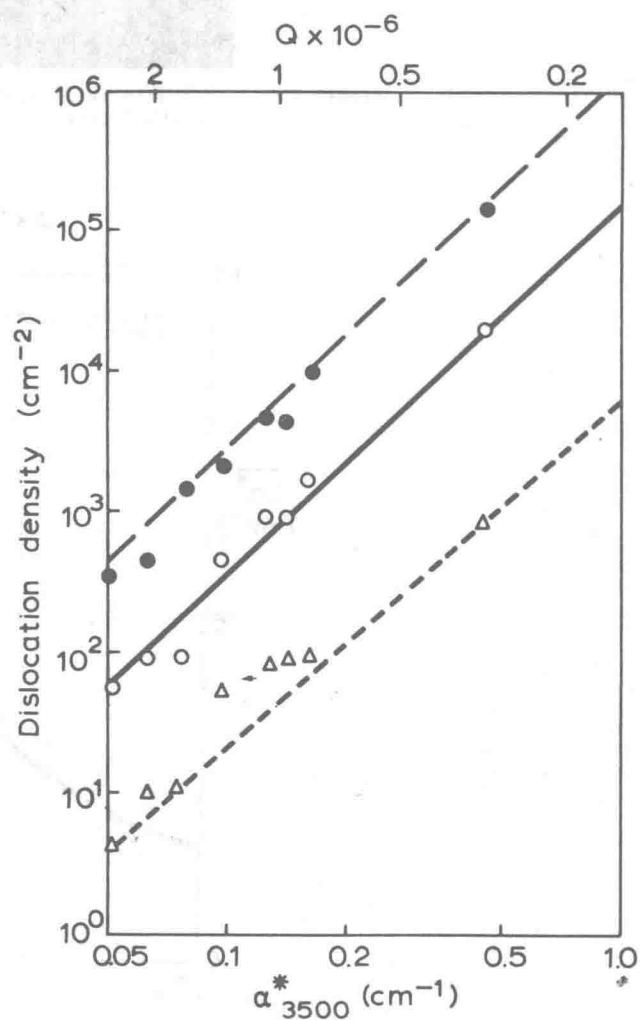


Figure 8. Dislocation density as a function of α^* . The full line is median values. The broken lines represent maximum and minimum observed values.