TEMPERATURE VARIATION OF THE 
REFRACTIVE INDICES OF QUARTZ

BY T. RADHAKRISHNAN
(From the Department of Physics, Indian Institute of Science, Bangalore)

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1. INTRODUCTION

The variations of the refractive indices of quartz with temperature present some interesting features. At the shortest wave-length (about $\lambda$ 2000) at which measurements are available, both the ordinary and extraordinary indices increase with rising temperature. On the other hand, in the visible spectrum, the temperature coefficients are negative and become numerically larger as the wave-length is increased. The temperature coefficients of the extraordinary and ordinary indices differ considerably throughout, much more so than the indices themselves.

In the present paper, a quantitative explanation of these features is offered on the basis of a theory recently put forward and applied with success to several isotropic solids by Mr. G. N. Ramachandran (1947). Ramachandran pictures the change in refractive indices due to an increase in temperature as arising from a superposition of the following effects:—

(A) a diminution due to the decreased number of oscillators per unit volume as the crystal expands.

(B) an increase, due to the shift towards longer wave-lengths of the characteristic ultra-violet absorptions.

In the particular case of vitreous silica, discussed in detail by Ramachandran, the thermal expansion, and therefore the effect (A) is nearly negligible, so that we have a steady increase of refractive index with rising temperature. On the other hand, in crystalline quartz, both effects have to be considered and effect (A) is greater than (B) for wave-lengths longer than $\lambda$ 2100, thereby making the temperature coefficients negative.

2. THE DISPERSION FORMULAE OF QUARTZ

Accurate measurements of the temperature coefficients extend over the region $\lambda$ 2000 to $\lambda$ 6500. In this region, the dispersion of both the indices is principally determined by an ultra-violet characteristic frequency, which
was first calculated by Rubens (1897) from the dispersion data to be in the neighbourhood of λ 1000. Subsequently, Lowry and Coode-Adams (1927–28) showed that the refractive dispersion as well as the dispersion of optical rotatory power, could be accurately explained by a term at λ 1127. Recently (1936) Tousey has shown experimentally that quartz exhibits two maxima of selective reflection at λ 1190 and λ 1060. The choice of λ 1127 which is nearly a mean of these two, is thus seen to be a happy one, and it explains the refractive indices with sufficient accuracy for our purpose. In addition, there are contributions to refraction from infra-red and remote ultra-violet terms. The contributions of the infra-red terms are very small in the region under consideration, so that variations due to a shift in the infra-red characteristic frequencies are negligible. The contributions from the remote ultra-violet arise from purely atomic transitions in silicon and oxygen. The characteristic frequencies, therefore, cannot be expected to change with temperature. Consequently, the purpose of investigating the temperature coefficients would be satisfied by dispersion formulæ which stress the importance of the term at λ 1127 and express the contributions by the other terms in as simple a manner as possible. Such formulæ have been obtained here as simplifications of formulæ originally proposed by Coode-Adams. They are,

\[ n_\omega^2 = 1.7239 + 0.002682 \nu^2 + \frac{49.630}{78.436 - \nu^2} - \frac{0.0109}{\nu^2} \]  
(1)

\[ n_\epsilon^2 = 1.7210 + 0.002761 \nu^2 + \frac{51.962}{78.436 - \nu^2} - \frac{0.0109}{\nu^2} \]  
(2)

The agreement of these formulæ with the facts is set out below, in Table I.

<table>
<thead>
<tr>
<th>Wavelength (microns)</th>
<th>( n_\omega ) (calculated)</th>
<th>( n_\omega ) (observed)</th>
<th>( n_\epsilon ) (calculated)</th>
<th>( n_\epsilon ) (observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20255</td>
<td>1.6453</td>
<td>1.6456</td>
<td>1.6580</td>
<td>1.6584</td>
</tr>
<tr>
<td>0.31227</td>
<td>1.5742</td>
<td>1.5743</td>
<td>1.5944</td>
<td>1.5945</td>
</tr>
<tr>
<td>0.467815</td>
<td>1.5510</td>
<td>1.5510</td>
<td>1.56035</td>
<td>1.56037</td>
</tr>
<tr>
<td>0.64485</td>
<td>1.5423</td>
<td>1.5423</td>
<td>1.5512</td>
<td>1.5513</td>
</tr>
</tbody>
</table>

This degree of agreement, though not as perfect as that to be expected of a regular dispersion formula, is sufficiently good for the present purpose,
3. Application

Formulæ (1) and (2) are of the form

\[ n^2 = a + c v^2 + \frac{b}{v_0^2 - v^2} - \frac{e}{v^8} \]

\[ = a + f(\rho, v_0), \quad (3) \]

where \( \rho \) is the density of the crystal. If \( t \) be the temperature,

\[ 2n \frac{dn}{dt} = \frac{df}{d\rho} \frac{d\rho}{dt} + \frac{df}{dv_0} \frac{dv_0}{dt}. \quad (4) \]

In this form of dispersion formula, the oscillator strengths \( b, c \) and \( e \) are simply proportional to the density of the crystal, so that the dependance of \( f \) on \( \rho \) can be written as

\[ f(\rho) = \rho, \quad (5) \]

where \( k \) is a constant.

\[ \Rightarrow \frac{\partial f}{\partial \rho} \frac{d\rho}{dt} = k \frac{df}{d\rho} = -k \gamma_\rho = -\gamma_t \rho \]

\[ = -\gamma_t (n^2 - a), \quad (6) \]

where \( \gamma_t \) is the coefficient of cubical expansion at the temperature \( t \). Also

\[ \frac{\partial f}{\partial v_0} \frac{dv_0}{dt} = -2b v_0 \frac{dv_0}{dt} \]

\[ \frac{\partial f}{\partial v_0} = - \frac{2b v_0}{(v_0^2 - v^2)^2} \frac{dv_0}{dt} \]

Let us write, for convenience,

\[ \frac{d}{dt} \frac{d v_0}{dt} = \frac{1}{v_0} \frac{dv_0}{dt} = x_t, \]

\[ (7) \]

where \( x_t \) itself can be a function of temperature. Substituting (6) and (7) in (4), we get

\[ 2n \frac{dn}{dt} = \frac{da}{dt} - \gamma_t (n^2 - a) - \frac{2b v_0^2}{(v_0^2 - v^2)^2} x_t \]

\[ 2n \frac{dn}{dt} = A + \frac{B x_t}{(v_0^2 - v^2)^2} \quad (8) \]

where

\[ A = \frac{da}{dt}; \quad B = -2b v_0^2. \]

Applying these to the two indices, we get

\[ 2n_w \frac{dn_w}{dt} + \gamma_t (n_w^2 - a_w) = A_w + \frac{B_w x_t}{(v_0^2 - v^2)^2} \]

\[ 2n_e \frac{dn_e}{dt} + \gamma_t (n_e^2 - a_e) = A_e + \frac{B_e x_t}{(v_0^2 - v^2)^2}. \]
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Thus, if the left-hand sides of both these equations are computed, and plotted against \( \frac{1}{(v^2 - \nu^2)^2} \), two straight lines should be obtained, whose slopes should give \( B_\nu X_t \) and \( B_\nu X_r \) and whose y-intercepts should give \( A_\nu \) and \( A_\nu \). This was actually done, using Micheli's experimental values of \( \frac{dn_\nu}{dt} \) and \( \frac{dn_\nu}{dt} \) reduced to vacuum, and at a mean temperature of 60° C. The graphs were both straight lines, thus verifying the theory, and Micheli's data were found to be well expressed by the following formulas:

\[
2n_\nu \frac{dn_\nu}{dt} + 35.6 \times 10^{-6} (n_\nu^2 - 1.7239) = -36.23 \times 10^{-6} + \frac{0.227}{(78.44 - \nu^2)^2} \quad (9)
\]

\[
2n_\nu \frac{dn_\nu}{dt} + 35.6 \times 10^{-6} (n_\nu^2 - 1.7210) = -40.43 \times 10^{-6} + \frac{0.238}{(78.44 - \nu^2)^2} \quad (10)
\]

The values of \( \chi_r \), computed from (9) and (10) are

\[
\chi_r = - \frac{0.227}{2 \times 49.63 \times 78.44} = -2.92 \times 10^{-4}
\]

\[
\chi_t = - \frac{0.238}{2 \times 51.96 \times 78.44} = -2.92 \times 10^{-4}
\]

The values derived from the temperature-variations of the ordinary and extraordinary indices thus agree perfectly. The values of the temperature coefficients, calculated from (9) and (10) are compared with the experimental values in Table II and the graph (Fig. 1) shows theoretical curves of \( \frac{dn}{dt} \) against \( \lambda \) with the experimental points marked side by side.

No systematic error is seen. The value of \( \chi_t \) is of the same order of magnitude as Ramachandran's value \((-2.5 \times 10^{-6})\) for \( \frac{d \log \nu}{dt} \) of the characteristic frequency at \( \lambda \) 1070 in vitreous silica.

### Table II

<table>
<thead>
<tr>
<th>Approx. wavelength (microns)</th>
<th>( \frac{dn_\nu}{dt} \times 10^6 ) (calculated)</th>
<th>( \frac{dn_\nu}{dt} \times 10^6 ) (observed)</th>
<th>( \frac{dn_\nu}{dt} \times 10^6 ) (calculated)</th>
<th>( \frac{dn_\nu}{dt} \times 10^6 ) (observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.202</td>
<td>+1.85</td>
<td>+1.84</td>
<td>+1.28</td>
<td>+1.29</td>
</tr>
<tr>
<td>0.207</td>
<td>+2.81</td>
<td>-3.09</td>
<td>-3.67</td>
<td>-3.89</td>
</tr>
<tr>
<td>0.312</td>
<td>-4.94</td>
<td>-4.68</td>
<td>-5.50</td>
<td>-5.68</td>
</tr>
<tr>
<td>0.340</td>
<td>-5.02</td>
<td>-5.08</td>
<td>-6.00</td>
<td>-6.17</td>
</tr>
<tr>
<td>0.487</td>
<td>-6.08</td>
<td>-5.06</td>
<td>-7.14</td>
<td>-7.15</td>
</tr>
<tr>
<td>0.508</td>
<td>-6.26</td>
<td>-6.26</td>
<td>-7.29</td>
<td>-7.29</td>
</tr>
<tr>
<td>0.643</td>
<td>-8.56</td>
<td>-6.60</td>
<td>-7.64</td>
<td>-7.64</td>
</tr>
</tbody>
</table>
The temperature coefficients \( \left( \frac{dn}{dt} \right) \) and \( \left( \frac{dn}{dt} \right) \) themselves vary with the temperature and we shall seek now to explain the variations on the basis of this theory. From our formula

\[
2n \frac{dn}{dt} + \gamma_t (n^2 - a) = A_t + \left( \frac{Bx_t}{\nu_0} \right)^2
\]

we get

\[
x_t = \left( \frac{\nu_0^2 - \nu^2}{\nu} \right)^2 \left[ 2n \frac{dn}{dt} + \gamma_t \left( n^2 - a - \frac{A_t}{\gamma_t} \right) \right]
\]

Since \( A_t = \frac{da}{dt} \) and \( a \) is partly a constant and partly proportional to the density, we can write \( \frac{A_t}{\gamma_t} \) constant and this constant can be determined, knowing \( A_t \) at any temperature. Hence, if \( \left( \frac{dn}{dt} \right) \) is known for various temperatures, \( x_t \) can be evaluated as a function of temperature. The best data on \( \left( \frac{dn}{dt} \right) \) as a function of \( t \) are those of Reed (1898). His values for the
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ordinary ray at 60° C., however, differ systematically from the values of Micheli, on which the present formulæ are based. There is, on the other hand, good agreement in the case of the extraordinary ray. Calculations have hence been confined to the extraordinary ray.

On substituting numerical values in (11), the following formulæ result:

\[
\begin{align*}
-x_t &= 2.0535 \left( \frac{dn_x}{dt} \right)_{\lambda=4358} + 1.2155 \gamma_t \\
-x_t &= 2.1760 \left( \frac{dn_x}{dt} \right)_{\lambda=5893} + 1.2155 \gamma_t \\
-x_t &= 2.2067 \left( \frac{dn_x}{dt} \right)_{\lambda=6563} + 1.2970 \gamma_t
\end{align*}
\]  

The values of \( x_t \) calculated from these formulæ are given below:

| Temperature (degrees C.) | \( \gamma \times 10^5 \) | \( \frac{dn_x}{dt} \times 10^6 \) (Red) | \( -x_t \times 10^3 \) |
|--------------------------|--------------------------|-------------------------------|----------------|----------------|----------------|----------------|
|                          |                          | 4358 | 5893 | 6563 | 4358 | 5893 | 6563 |
| 23.0                     | 34-35                    | -6.52 | -7.14 | -7.18 | 2.84 | 2.84 | 2.87 |
| 61.2                     | 35-6                     | -7.07 | -7.60 | -7.73 | 2.88 | 2.89 | 2.91 |
| 125.2                    | 37.7                     | -7.71 | -8.29 | -8.43 | 3.00 | 3.02 | 3.05 |
| 177.0                    | 39.35                    | -8.73 | -9.33 | -9.44 | 2.99 | 3.01 | 3.02 |
| 227.5                    | 41.1                     | -9.52 | -10.12 | -10.30 | 3.05 | 3.06 | 3.06 |
| 275                      | 42.5                     | -11.06 | -11.78 | -11.91 | 2.91 | 2.90 | 2.90 |
| 328                      | 44.7                     | -13.48 | -14.19 | -14.27 | 2.86 | 2.85 | 2.85 |
| 385                      | 47.3                     | -17.03 | -18.40 | -18.57 | 2.15 | 2.05 | 2.03 |
| 435                      | 49.95                    | -21.49 | -22.95 | -22.75 | 1.66 | 1.49 | 1.46 |

Several interesting features are observed about this table. In the first place, the values of \( x_t \) calculated from various wavelengths for the same temperature agree very well, thus confirming the soundness of the theory. \( x_t \) is constant till about 300° C., and the value of \( 3 \times 10^{-5} \) is the same as that calculated from the work of Nedungadi (1940) on the temperature variation of the fundamental Raman frequency shift 465 cm\(^{-1}\) in quartz, over the same range of temperature. This again illustrates the correspondence between electronic and lattice vibrations noticed by Ramachandran for a number of other substances. After 300° C., however, the value of \( x_t \) falls off, contrary to the behaviour of the Raman line.

I express here my thanks to Sir C. V. Raman for his guidance in this piece of work.
5. Summary

The temperature variation of the refractive indices of quartz has been quantitatively explained on the basis of a theory put forward by G. N. Ramachandran and all the features observed, viz., the reversal in sign of the coefficients in the ultra-violet, the variation of the coefficients with temperature and the difference between the coefficients for the extraordinary and ordinary rays are satisfactorily accounted for. The rate of shift with temperature of the characteristic ultra-violet frequencies of quartz near $\lambda 1127$ has been calculated for various temperatures. At about $60^\circ$ C. $d (\log v)/dt = -2.92 \times 10^{-8}$ which agrees with Nedungadi's value of $-2.87 \times 10^{-8}$ for $d (\log v)/dt$ of the fundamental Raman frequency 465 cm.$^{-1}$ in quartz at that temperature, and is of the same order as Ramachandran's value of $-2.5 \times 10^{-8}$ for $d (\log v)/dt$ of the ultra-violet absorption frequency at $\lambda 1070$ in vitreous silica.

References