A SPECTROPHOTOMETRIC STUDY OF SMOKY QUARTZ

Nora M. Mohler, *Smith College,*
Northampton, Mass.

Abstract

The absorption curve of smoky quartz was determined from 700 to 200 $m\mu$; this was compared with its absorption after decoloration by heat and exposure to radium, and with clear crystalline and fused quartz colored by the same exposure. Some fluorescence effects were noted. All showed maxima at 16,500, 20,000, 25,000, 33,000, 38,000 (wave number per cm.), with increased absorption beyond 42,000. Further irradiation in general simply increased absorption, but fused quartz showed a shift in importance of the bands, with a superposed lavender tint. The similarity in curves of originally smoky and the irradiated specimens confirms the theory of radioactive coloration.

The change in energy due to the transfer of an electron from an oxygen to a silicon ion is calculated, and possible subsequent changes due to redistribution of such electrons. These changes correspond to amounts of energy indicated by positions of absorption bands.

Clear quartz colored by exposure to radioactive action is similar in appearance to naturally colored smoky quartz; their absorption curves in the visible region were compared by Holden[1] in his study of the causes of this color. The following experiment extends the comparison to 200 $m\mu$.

Experimental Procedure and Results

Spectrograms of several pieces of smoky quartz were taken with a Hilger E3 spectrograph, used in conjunction with a Gaertner rotating sector photometer, and as a light source a hydrogen discharge tube run by a 1 kw. transformer was used. The specimens were placed near the slit of the spectrograph, in the lower beam from the photometer.[2] Due to the irregular variations in absorption which occur in naturally colored specimens, a sufficiently complete series for a curve was taken on each plate, as well as a test strip without the absorbing material. Points of equal density on the standard and absorbed strips were estimated visually; the probable error of these readings was found to be less than 1%.

The absorption curves plotted from these results showed identical positions of maxima for the different specimens. The one given (Fig. 1) is from a piece cut from a deeply colored crystal from Florissant, Colorado; it was cut with plane, parallel faces, and with a thickness of .23 cm.

---

[1] Holden, E. F., The cause of color in smoky quartz and amethyst: *Am. Mineral.*, vol. 10, p. 203, 1925.

[2] Mohler, N., Ultra-violet absorption of certain minerals: *Am. Mineral.*, vol. 16, p. 300, 1931. The spectrum with the E3 spectrograph is about 8″.

This specimen was decolored by heating to 300°C. for 15 minutes; then it, together with a piece of clear crystalline quartz of optical quality (thickness .47 cm.) and a piece of fused quartz (.20 cm.) cut from a drawn rod, were exposed for 92 days to the gamma rays from 100 mg. of radium. All showed the typical smoky color. Spectrograms taken at once showed fluorescence in the ultra-violet; those taken later yielded absorption curves similar to that of the naturally colored smoky quartz (Figs. 1, 2, 3).

A second exposure, to 200 mg. of radium for 140 days, was then made, part of the time to beta and gamma rays. A more intense smoky color was produced, especially in the parts affected by the beta rays; the fused quartz showed a lavender tint on the smoky background. Spectrograms were taken as before, and also with an alanine filter. As this cuts at 200 $m\mu$ and the fused quartz window of the discharge tube at 190 $m\mu$, the wave length of the fluorescence-exciting radiation was limited sufficiently to permit a rough estimate of the shift in wave length. The resulting curves are given in Figs. 1, 2, 3, 4.

The results for all of the crystalline specimens, whether naturally or artificially colored, show maxima at 16,500, 20,000, 25,000, 33,000, 38,000 (wave number per cm.) with increased absorption beyond 42,000. The similarity offers strong confirmation to the hypothesis of coloration by radioactive action.

THEORETICAL DISCUSSION

Theories proposed to explain this action[3,4] assume a transfer of electrons to new positions as a result of radioactive bombardment, with either their subsequent return or a coagulation of ions into colloid particles. A calculation of the order of magnitude of forces involved in the first of these assumptions follows. The crystal energy due to Coulomb binding forces and a repulsive force effective at small distances is given by the equation:

$$\phi = -\frac{z^2 e^2 A}{r} + \frac{B}{r^n}$$

in which ze is the charge on an ion, r a characteristic ionic distance, A the Madelung constant which depends on the magnitude and distances of the surrounding charges (assumed 2.44), n a constant which can be calculated from compressibility data (taken as 9), B a constant which can be eliminated by the condition that at equilibrium $r = R$, the experimentally found ionic distance. To simplify the calculation of the change

[3] Lind, S. C., and Bardwell, D. C., Coloring and thermophosphorescence produced in transparent minerals and gems by radium radiations: *J. Frank. Inst.*, vol. 196, p. 375, 1923.

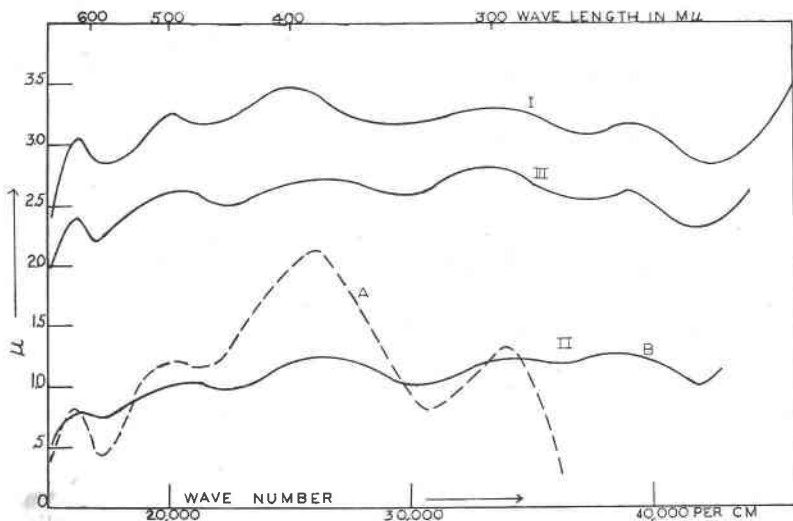[4] Przibram, Color changes and luminescence due to Becquerel rays: *Zeit. Phys.*, vol. 68, p. 403, 1931.

Fig. 1. Absorption curves of smoky quartz.

I. Naturally smoky quartz.
II. After decoloring by heat, followed by 92 days of irradiation with 100 mg.
   radium.
   A. Curve determined immediately.
   B. Curve determined 5 weeks later.
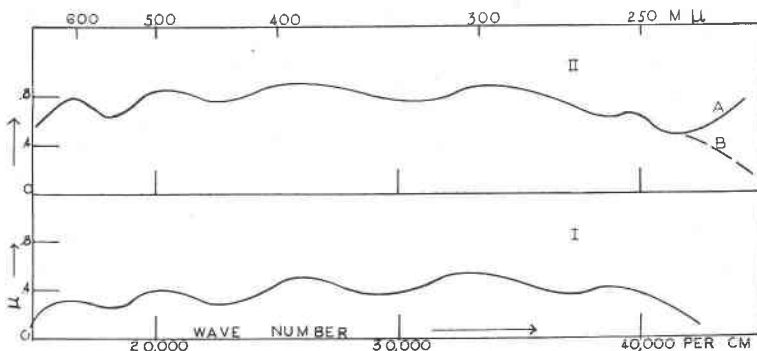III. After second irradiation for 140 more days, with 200 mg. radium.

Fig. 2. Clear crystalline quartz.

I. After first irradiation.
II. After second irradiation.
   A. Plates taken with alanine filter.
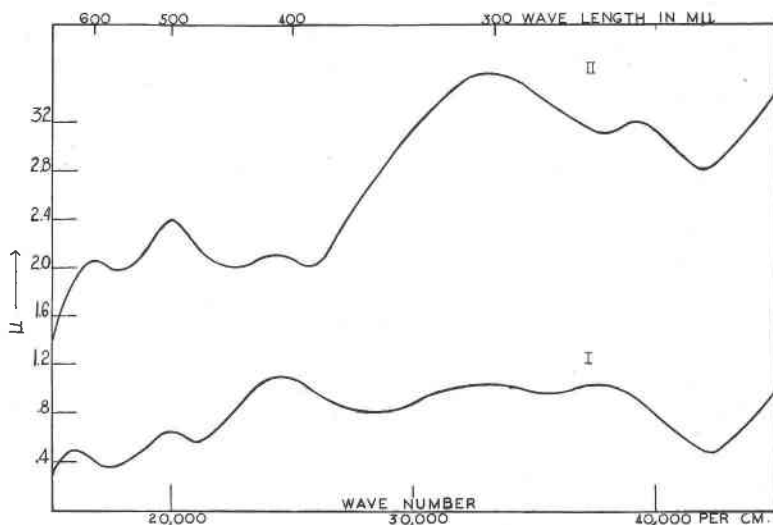   B. Plates taken without filter.

Fig. 3. Clear fused quartz.
I. After first irradiation.
II. After second irradiation.

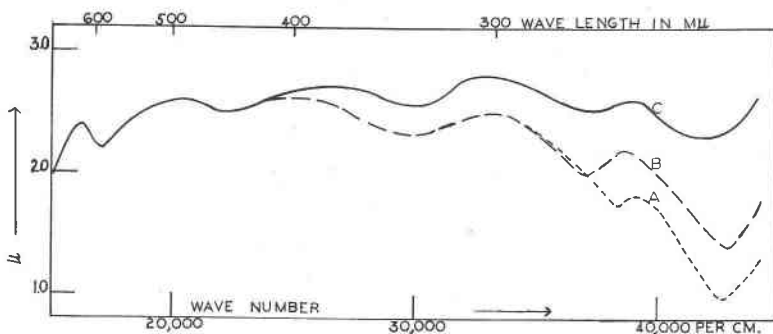

Fig. 4. Smoky quartz after second irradiation.
A. Curve taken at once without filter.
B. Curve taken at once with alanine filter.
C. Curve taken 5 days later, no filter.

introduced by a shift of one or more electrons, this may be written:

$$\phi = z\ e\ P, \text{ with } P = -2e(\sum 1/r_0 - \sum 2/r_{Si})(1-1/n).$$

For the value of r for beta quartz

$$\phi = -.889 \times 3.07\ e^2\ z.$$

The shift of an electron from an oxygen to a silicon ion would mean a change in z from 4 to 3; then the summation, if considered for an electrostatically neutral region, must be changed by $1/R$. For beta quartz $R = 1.61$; for alpha quartz, with which we are concerned, there are two values for R, as the oxygen tetrahedron is distorted. The possible values are given in Table 1. One series of energy changes correspond to changes in z, a second series corresponds to changes with z constant. The order of

TABLE 1. ENERGY LEVELS FOR A SILICON ION IN LOW QUARTZ

	A		B	
z	$\sum \frac{2}{r_O} - \sum \frac{4}{r_{Si}}$	$-\frac{\phi}{e^2}$	$\sum \frac{2}{r_O} - \sum \frac{4}{r_{Si}}$	$-\frac{\phi}{e^2}$
$4 \times .889 \times 3.07$		10.92		
$3 \times .889 \times 3.07 - .61$		6.55	$3.07 - .30$	7.38
$3.07 - .65$		6.37	$3.07 - .27$	7.46
			$3.07 - .25$	7.50
$2 \times .889 \times 3.07 - .61 - .61$		3.29	$3.07 - .61 - .30$	3.84
$3.07 - .61 - .65$		3.22	$3.07 - .61 - .27$	3.89
$3.07 - .65 - .65$		3.14	$3.07 - .61 - .25$	3.92
			$3.07 - .65 - .30$	3.76
			$3.07 - .65 - .27$	3.82
			$3.07 - .65 - .25$	3.86
$1 \times .889 \times 3.07 - .61 - .61$			$3.07 - .61 - .61 - .30$	1.38
$-.65$		1.07	$3.07 - .61 - .61 - .27$	1.41
$3.07 - .61 - .65$			$3.07 - .61 - .61 - .25$	1.42
$-.65$		1.03	$3.07 - .61 - .65 - .30$	1.34
			$3.07 - .61 - .65 - .27$	1.37
			$3.07 - .61 - .65 - .25$	1.39
			$3.07 - .65 - .65 - .30$	1.31
			$3.07 - .65 - .65 - .27$	1.33
			$3.07 - .65 - .65 - .25$	1.35

	C		D	
$2 \times .889 \times 3.07 - .30 - .27$		4.44		
$3.07 - .30 - .25$		4.47		
$3.07 - .27 - .25$		4.52		
$3.07 - .25 - .25$		4.56		
$1 \times .889 \times 3.07 - .61 - .30 - .27$		1.68	$3.07 - .30 - .27 - .25$	2.00
$3.07 - .61 - .30 - .25$		1.70	$3.07 - .30 - .25 - .25$	2.02
$3.07 - .61 - .27 - .25$		1.73	$3.07 - .27 - .25 - .25$	2.05
$3.07 - .61 - .25 - .25$		1.74		
$3.07 - .65 - .30 - .27$		1.64		
$3.07 - .65 - .30 - .25$		1.66		
$3.07 - .65 - .27 - .25$		1.69		
$3.07 - .65 - .25 - .25$		1.71		

magnitude of the first set is that of energy available in radioactive action; of the second, that of much smaller energy changes. The latter are grouped in Table 2, with their corresponding wave numbers, and the wave numbers of the regions of principal absorption.

TABLE 2

In A are grouped differences calculated from Table 1 for z constant, and shifts of a single electron only. In B are the wave numbers corresponding to these energies.
In C are the absorption maxima found experimentally.

A Energy changes	B Wave number per cm.	C Wave number of absorption maxima
.50–1.13 $-\dfrac{\phi}{e^2}$	58.0 -131×10^3	
not continuous		
.40–.46	46.4 –53.4	Above 43×10^3
.38–.22	44.1 –25.6	24–42, with maxima at 25, 34, 38
.18	20.9	20.5
.12	13.9	16.5
.01–.08	1.16– 9.29	Fluorescence shifts between 4.3 and 12

The hypothesis involved in these comparisons is that the initial disturbance caused by the radioactive action may be followed by rearrangements of electrons if the requisite energy is supplied. The results given, since corrections for readjustment in position of the ions are neglected, are of value only in indicating an order of magnitude. The agreement seems sufficient, however, to indicate that a further assumption of a coagulation of colloid particles is unnecessary to account for the color of smoky quartz.