

SPECTROSCOPIC STUDY OF AMETHYST QUARTZ IN THE VISIBLE REGION*

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Plate I

ABSTRACT. In this paper a detailed study is made of the absorption of light in the visible region by amethyst quartz. It is found that in the visible region, an absorption band, the so called F-band appears, which decreases in intensity at high temperature the maximum also shifts towards longer wavelengths; but the number of colour centres remain constant till about 200°C. At higher temperatures these centres, which are responsible for the absorption, are destroyed by heat. When the crystal is exposed to radiation absorbed by the F band, a new F'-band appears. The facts reveal that the coloration is due to exposure to some penetrating radiations.

INTRODUCTION

It has long been known that certain crystals, which are normally transparent, are found coloured in nature, and it has been found that these colours can also be produced artificially by physical means and by the addition of chemical impurities. Well known examples are those of the alkali halides which were thoroughly studied by Pohl and his collaborators. A good account of this work done by Pohl is found in two survey articles by Pohl (1937, 1938) and the more recent work can be found in a survey article by Seitz (1946).

The agencies which cause coloration of crystals may be broadly divided into two categories, chemical and physical. In the former may be included pigments, inclusion of foreign substances or even a small stoichiometric excess of one of the elements and in the latter purely physical processes are responsible for the coloration, the crystal remaining chemically pure. This discoloration may be due to exposure to ionizing radiations such as ultraviolet rays, X-rays and gamma rays or even cathode rays.

The coloured varieties of quartz have of late been investigated with a view to elucidating the cause of the coloration. It has been found that even the natural transparent crystals can be coloured. But so far no final solution has been obtained. In this paper a detailed study of the physical properties

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of the violet variety of quartz-amethyst quartz- is made in order to understand the nature of the coloration.

Coloured alkali halides and F-bands. A systematic study of these crystals was carried out by Pohl and his collaborators. They found that when these crystals are exposed to ultraviolet or heated in alkali metal vapour they become coloured. This coloration is due to the presence of characteristic absorption band which lies in the visible region. Pohl has called this absorption band the F-band, and the absorption centres F-centres (Farbzentren).

Coloured quartz. In addition to the transparent variety, quartz is also found coloured. We have the violet blue, yellow or citrine, rose and smoky varieties found in widely scattered countries and in the same area several other mixed varieties can be seen. Amethyst quartz is found in abundance in certain quartz reefs of the Deccan. The crystals are well formed and are usually violet, but some of them are translucent and appear to be similar to amethyst crystals bleached by heat. Sometimes crystals, which are partly violet and partly smoky, are found and this suggests a common origin of the two varieties.

Discoloration by X-rays and radium rays. Discoloration of transparent quartz, especially by X-rays was studied recently. The earliest to investigate the effect of radium rays seems to be Bensaude and Costanzo (1922), Lind and Bradwell (1923) and Hoffmann (1931). The results obtained by different investigators appear to be conflicting. Apparently, the colour developed depends on the impurities and the initial colour of the specimen. Futtagami (1938) obtained a smoky colour when the transparent crystal was exposed to X-rays, while Laemmlein (1944) got a violet colour. He found that some specimens remained colourless. While glass prepared from smoky quartz acquired an intense violet colour, pale amethyst quartz acquired only an additional faint smoky colour. A systematic study of the coloration produced by radium rays in different varieties of quartz was made by Choong (1945). His conclusions are the following :

1. All coloured crystals acquire a smoky colour when exposed to radium rays.
2. The same rays render vitreous quartz violet in colour instead of smoky.
3. The natural colours and those produced by radium rays in the quartz, both crystalline and vitreous can be eliminated by heating. The artificial smoky and violet tints fade with perceptible rapidity at 190°C and 300°C respectively. After heating, the specimens regain their original transparency and they can be coloured again. The time required for the decoloration depends greatly on the temperature and also on the nature of the colour.

Previous explanations of colour in coloured quartz. Several attempts have been made to explain the colour of amethyst quartz and other varieties. Holden (1925) is of the view that the colour of the smoky quartz is due to

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the atoms of silicon liberated by the action of rays of the radioactive substances during the long geological epoch. Mohler (1936) comes to the same conclusion in the case of smoky quartz. In a detailed investigation on the case of colour in blue quartz made by Jayaraman (1939) the conclusion reached is that the element responsible for the colour is titanium.

He suggests that the colour is only an opalescent colloidal one produced by colloidal particles of the size of 0.2 to 0.5 microns in diameter, modified by the absorption of titanium. Vedeneeva (1940), who studied absorption spectra for the ordinary and extra-ordinary rays in amethyst quartz, found a maximum at 5400 \AA and deduced that the colour may be due to highly dispersed inclusions, perhaps of ferric ions. Recently another attempt was made by Narayana Rao (1947) to find the cause of the coloration of amethyst. With that view he found its dielectric constant.

In the present investigation a detailed spectroscopic study of amethyst quartz in the visible region is made in order to find the cause of coloration.

PART I

ABSORPTION COEFFICIENTS AT DIFFERENT TEMPERATURES

Experimental study. After careful examination, one plate 2.3 millimetres thick was cut off from one of the faces. There was no sign of the presence of any streaks of colour or cracks, the specimen being uniformly coloured and free from inclusions. Another plate of amethyst quartz was obtained from a crystalline specimen picked up from an entirely different quartz reef. This plate was also cut in such a way that its plane made an angle of 33 degrees with optic axis of the crystal. The coloration for all practical purposes could be taken as uniform. This specimen was used for the study of the effect of heat on specimens of crystalline amethyst quartz in order to understand clearly how thermal treatment removes the coloration. In future, this specimen of the amethyst quartz shall be called A_2 and the former A_1 for the sake of convenience.

Amethyst quartz, by transmitted light has a reddish violet colour, and this shows that by a process of selective absorption, the other components of the electromagnetic spectrum between the red and violet region are absent (see Plate I,) partially or completely in the light after transmission. A spectrogram of the transmitted light was taken. Exposure of the order of ten minutes were given on Kodak panchromatic plates. The spectrum of the mercury arc was photographed above and below each spectrogram for purposes of comparison. All the spectrograms indicated an absorption band from the blue to the orange region near about the mercury line 5461 \AA . There were no other bands in the visible region.

QUANTITATIVE EVALUATION OF THE ABSORPTION
COEFFICIENT AT LIQUID AIR, ROOM AND HIGH
TEMPERATURES

The evaluation of the absorption co-efficient for different wavelengths were made visually by means of spectro-photometer of the Marten's type made by Bausch and Lomb. The source of light was a powerful 250-watt lamp. To enable limited regions of definite width into the field of view, a slit was placed in the eye-piece. This was of sufficient width to let in 20 Angstroms in the violet region of the spectrum.

The study of the absorption of amethyst quartz in the visible region was made also at both high and low temperatures using the spectro-photometer. For high temperature work the specimen was placed in a specially designed heater constructed in this laboratory. The heater consisted of a cylindrical block of brass with an internal bore of diameter 2.5 cm. In this another hollow cylinder, with a rectangular enclosure in the centre for holding the specimen, fitted exactly. The specimen could be held firmly in the holder by means of a sliding tube, the axis of which was in coincidence with that of the external cylinder. This was arranged in such a way that the crystal would not experience any undue pressure. At right angles to the axis of the system, an aperture was made for holding the thermometer. This thermometer was used only in the temperature range $0^{\circ}\text{C}-350^{\circ}\text{C}$ when it was placed in position it would always be in actual contact with the specimen under study. The surface of the entire cylinder was first covered with a thin layer of asbestos over which was wound nichrome wire, and finally set in a mixture of plaster of paris asbestos flakes. The resistance coils were fed by A. C. from a variac 0-270 volts.

In making absorption measurements at room temperature, the crystal was mounted against an aperture in a cardboard in such a way that stray light would not pass through the sides. This mounting was then held against one of the rhomboid prisms and readings were taken.

For the purpose of making observations at the temperature of liquid air, a three walled Dewar flask was placed in position before the rhomboid prisms and liquid air was poured into it. The solid specimen was fixed in one of the two apertures of a brass rod provided for the entrance and exit of the two light beams. Enough liquid air had to be poured into the Dewar flask so that the surface of the liquid may be well above the two apertures. With this type of arrangement the specimen attained the temperature of liquid air within a few minutes.

RESULTS

The respective calculated absorption co-efficients of the specimen at different temperatures for different wavelengths (given in electron volts)

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in the visible region are diagrammatically represented in figure 1.

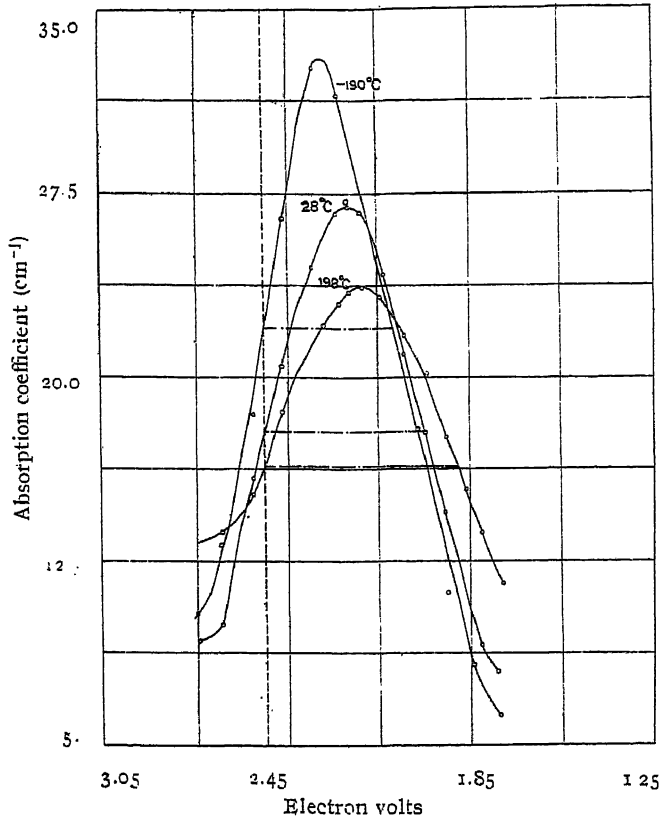


FIG. 1

Variation of the structure the of F-band with temperature

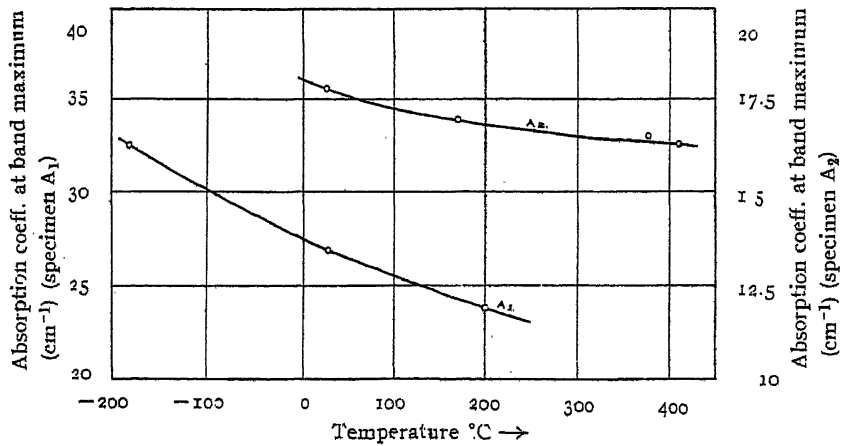


FIG. 2

Variation of absorption coefficient at band maximum in amethyst quartz with temperature

In confirmation of the results obtained from a study of absorption spectra by photographic methods, the spectro-photometric results revealed

a single bell shaped band with a maximum at 5500 Å. As the temperature of the specimen decreases it will be observed that the band narrows down, the width of the band at half maximum having shortened considerably.

The band maximum shifts towards shorter wavelengths with decreasing temperature. The long wavelength foot also simultaneously drops down in absorption values. As seen later, this process of cooling to low temperatures may not be capable of converting this absorption band into a narrow line or increase its absorption co-efficient to infinite values when brought near -273°C . This is shown diagrammatically in figure 2, where the absorption co-efficients of the band maxima for the two specimens of amethyst quartz (A_1) and (A_2) are plotted for different temperatures.

It will be seen that the graph becomes asymptotic only at high temperatures and that low temperatures do not effectively increase the absorption values.

TABLE I

Structural details of F-bands for different temperatures

Temp. °C	Band maximum in A. U.	Absorption co-efficient of band max	λ in A. U.		Width at half maximum in electron volt.
			vio.	red.	
-190	5270	33.00	4900	5890	0.424
+28	5500	26.92	4900	6130	0.530
+198	5600	23.87	4900	6542	0.634

Table I summarises the behaviour of the various structural details of the single band with temperature. Further, as we proceed from the short wavelength foot of the band towards the band maximum, the points on the short wavelengths slope having values of absorption co-efficient equal to half values of those in the absorption maximum, can be seen to arrange themselves in a line indicating that they are always at the same wavelength. (4900 Å), shown by the dotted line in the figure 1, no matter what the temperature is. A similar result was obtained by Mollow (1933) in the case of potassium bromide. This is ascribed to a transition between two undisturbed energy levels of the crystal.

PART II

OPTICAL EXCITATION OF AMETHYST QUARTZ

Experimental technique. To study in detail the absorption curve of amethyst quartz when excited, we must have the absorption curve of the specimen when excited so that a proper comparison can be made. As the absorption at room temperature has already been studied the data can be

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taken as that of the unexcited absorption curve, but there is a remote possibility that the green light of the incoming radiation may excite the F-centres a little without much interference from the red and infra-red passing through simultaneously. As such, it was considered worth while to take fresh readings of the absorption curves, taking care to quench the excitation if any such thing exists.

For this study the spectro-photometer was used again. The specimen was held in an aperture made in a card board and placed before a rhomboid prism of the photometer. A circular coil of thin constantan wire was placed in front of the crystal in such a way that it allowed light to traverse the specimen without any obstruction. This was made to glow appreciably by passing a strong current from a set of accumulators. The crystal was thus given a constant irradiation of infra-red light.

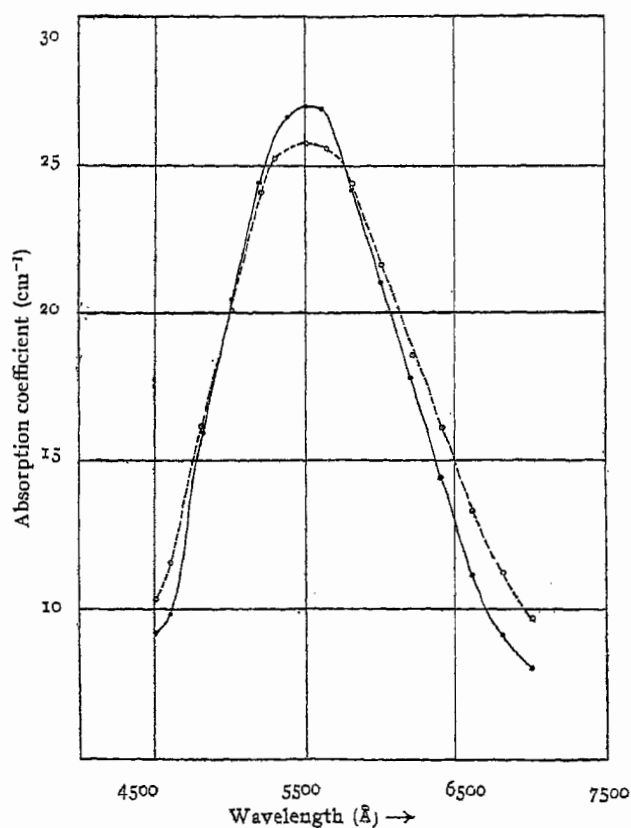


FIG. 3
Excitation of the Farbzentren in amethyst quartz
—o—o— unexcited
--o--o-- excited

To produce excitation, it is necessary to irradiate the specimen with light in the short wavelength foot of the absorption band, or in the band

maximum. In the case of amethyst quartz, a filter was used to transmit light of range between 4300 Å and 5200 Å. Intense white light from a 250-watt lamp was allowed to pass through a water cell in order to absorb completely the infra-red and then condensed on the crystal after passing through the blue filter. This flooding with blue light was the source of excitation and this was done between every two readings.

RESULTS

In figure 3, the corresponding absorption co-efficients calculated from these data are plotted against the wavelengths recorded in A. U. From the figure we see that the main features of excitation *viz*, the decrease in value of absorption co-efficient of band maximum and the increase in absorption of the long wavelength foot of the absorption band, are found in this case. The new absorption band has an absorption co-efficient of 25.68 cm⁻¹ in the band maximum as compared with 26.92 cm⁻¹ in the unexcited F-band. The unexcited band had values of absorption co-efficient the same as those for absorption at room temperature. Also at 7000 Å, the F-band has value of 8.09 cm⁻¹ while the F'-band has one at 9.73 cm⁻¹. An increase in value of absorption co-efficient in the short wave-length foot is also seen.

Refractive index of amethyst quartz. The measurements of refractive index of the specimen of amethyst quartz (A₁) were carried out using a Pulfrich refractometer. With the mercury arc in position the angles of emergence were measured for 4358 Å, as well as for the D₁ D₂ lines of sodium, for which purpose a sodium lamp is used. The calculated values of the refractive indices are given in Table II, and values of crystalline quartz being given for the sake of comparison. It will be seen that the results reveal the presence of slight anomalous dispersion in the region of the band.

TABLE II

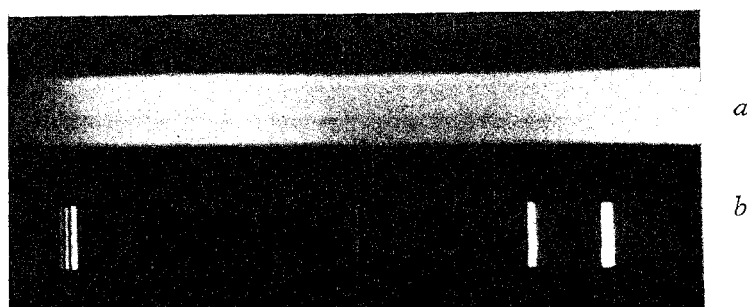
Wavelength in A. U.	Refractive index of amethyst quartz	Refractive index of crystalline quartz
5893	1.54924	1.5443
5461	1.54382	1.5462
4358	1.53858	1.5538

Number of centres.

The theory of dispersion by Smakula (1930) can be applied to F-centre bands in order to determine the density of these centres. It may be recalled that these bands probably arise from the excitation of electrons in vacant sites in crystals. As the electrons are coupled to the lattice the observed bands are much wider than lines of free atoms at room temperature.

According to Smakula

$$N_0 = \frac{18\pi}{\pi e^2 h} \cdot \frac{n_0}{(n_0 + 2)^2} \cdot K_{max} W.$$



The F band in amethyst quartz

- (a) Absorption spectrum of amethyst quartz (specimen A₃)
- (b) Comparison spectrum of the mercury arc.

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where N_0 is the number of absorbing centres, e , h and m are the usual atomic constants, n_0 the refractive index in the centre of the band, K_{max} , the absorption co-efficient of the band maximum and W the width of the absorption band at half maximum expressed in electron volts. Substituting the following values

$$\begin{aligned} e &= 4.803 \times 10^{-10} \text{ e. s. u.} \\ m &= 0.910 \times 10^{-27} \text{ grams.} \\ h &= 6.55 \times 10^{-27} \text{ erg. sec.} \\ n_0 &= 1.5438. \\ K_{max} &= 26.92 \text{ cm}^{-1}. \\ W &= 0.53 \text{ electron volts.} \end{aligned}$$

we get $N_0 = 6.05 \times 10^{15}$. It will be noted that the value given for n_0 is the value of the refractive index at the mercury wavelength 5461 Å.

The values of N_0 for the three different temperatures +198°C, +29°C and -190°C are given in Table III and the respective deviations of the number of F centres at -190°C and those at +198°C, from the number of centres at room temperature are also entered.

It will be found that the deviation at -190°C is of the order of 3.2% from the value at 28°C while that at 198°C is of the order of 6.8%. In calculating the values of N_0 the refractive index of the band maximum was assumed to be the same as that at the wavelength 5461 Å, at room temperature.

Number of F-centres for different temperatures at which colour is stable.

TABLE III

Temperature.	No. of centres.	Deviation in n_0 from 28°C.	Per cent deviation.
-190°C.	5866×10^{15}	190×10^{15}	3.2.
+28	6056×10^{15}	0.0×10^{15}	0.0.
+198	6424×10^{15}	368×10^{15}	6.0.

The deviations increase slightly with temperature showing thereby that by change of temperature, within limited ranges, a slight change is brought about in the number of F-centres. This can be taken as a further indication that the electron distribution confirms to classical statistics.

Decolorisation of amethyst by heat. The removal of F-centres has been made in various ways. The common way of removing these is by thermal treatment. When the crystal containing F-centres is heated at very high temperature the colour fades away. The speed of this process, *viz.* the loss in colour, depends essentially upon the temperature of the surroundings. The temperature at which all traces of colour vanish varies with the substance

under consideration. Amethyst quartz loses colour slowly at 300°C and quickly at temperature between 400°C and 450°C. The removal of colour in amethyst quartz was done by heating the specimen at high temperatures and the shape or the structure of the F-band observed at different stages.

The spectrophotometer was used again for determining the structure of the F-band when the specimen (A₂) was maintained at different temperatures for different intervals of time. After obtaining the absorption curve at room temperature, the absorption curve was obtained after tempering the specimen in the heater described before at a constant temperature of 380°C. Later, the specimen was placed in a sand bath and heated to 450°C and then brought down to room temperature and the absorption curve was determined. It was again maintained at 450°C for some time and brought back to room temperature. The temperature in this case was measured by a calibrated copper-constantan thermocouple. In this way a spectroscopic analysis was made of the loss of colour in amethyst quartz due to heating.

RESULTS

The spectrophotometric results are shown in figure 4. When maintaine.

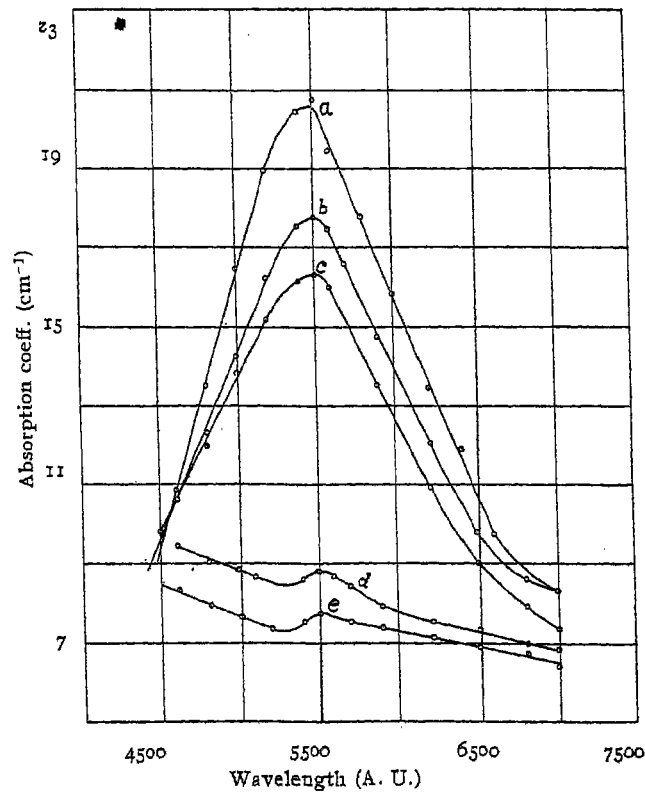


FIG. 4

Effect of tempering on the F band

at constant temperature of 380°C, a slow drop in absorption was noted.

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The maximum of the absorption band had an absorption co-efficient of 20.68 cm^{-1} at 380°C (curve *a*). Fifteen minutes after this reading was noted, the new value of the absorption co-efficient was 19.33 cm^{-1} . After another fifteen minutes the new value of the band maximum was 18.88 cm^{-1} . It will be seen from this that when maintained at 380°C for a period of a number of hours, the process of the dropping of absorption value might continue until the specimen loses its colour completely. Curves (*b*) and (*c*) in figure 4, were obtained when the specimen was maintained at temperature of 380°C for one and two hours respectively.

Curve (*d*) was obtained when the temperature was raised to 450°C and maintained for 30 minutes, while curve (*e*) is the result of heating at 450°C for 20 minutes after curve (*d*) was obtained. No trace of any colour could be seen when readings on curve (*d*) were being taken. Table IV summarises the structural details of the F-bands after tempering. It is interesting to note that even when no trace of colour was found in the specimen when curves (*d*) and (*e*) were taken, there are a few F-centres still existing, as evidenced by the humps in the respective curves.

TABLE IV
Structural details of the F-band after tempering

Curve No	Temp. of tempering $^\circ\text{C}$	Time of tempering	λ of band max.	K of band max.	λ_1	λ_2	Width at half max.	No of centres $\times 10^{15}$
<i>a</i>	28	0 mins	5480	20.6	4875	6100	0.510	4460
<i>b</i>	380	60 ,,	5500	17.69	4875	6050	0.540	4054
<i>c</i>	380	120 ,,	5500	16.25	4850	6000	0.493	3399
<i>d</i>	450	30 ,,	5500	8.75	5400	5700	0.120	455.7
<i>e</i>	450	50 ,,	5525	7.75	5400	5650	0.100	319.0

When the crystal containing F-centres is heated the centres acquire thermal energy as a result of which they move back to their former places and recombine. This recombination depends upon the amount of thermal energy acquired which in turn depends on the temperature at which the specimen is maintained. This is why the colour vanishes quickly at high temperatures than at lower temperatures.

DISCUSSIONS

In the case of the ionic crystals the discoloration could be produced by ultraviolet light or X-rays. But in the case of quartz, which at ordinary temperatures cannot be considered ionic to the same extent as potassium chloride, a more penetrating radiation is required to produce an

F-band. This is shown by the work of Choong (1945). That the intensity of coloration is greater in the case of fused quartz may mean that in this case there may be a slight stoichiometric excess of one of the elements, or an impurity present may also induce the formation of F-centres. This can be decided by the study of the other coloured varieties of quartz. In amethyst quartz studied here, it is found from a chemical analysis that iron is found in the ferric form. It was also found that the coloration of quartz takes place when the crystal is exposed to ultraviolet radiation coming from the flourite window of hydrogen discharge lamp.

Mott and Gurney (1940) have shown that from the theoretical point of view, a broadening $h\Delta\nu = \sqrt{h\nu_0 kT}$ is to be expected *i.e.* the breadth of the band at half maximum is proportional to the square root of the absolute temperature. This relation has been found to be valid approximately in the case of amethyst quartz. Table I leads to a similar conclusion.

It is known from the crystal structure of quartz (Mekeenan, 1923) that a silicon atom is surrounded by four oxygen atoms and each oxygen atom by two silicon atoms. But oxygen atom instead of having electrons for binding, actually lacks two electrons from a complete *p*-shell. These holes may be treated like positively charged electrons. Hence we say that the silicon oxygen bond occurs between a directed valence electron of silicon and a directed hole of oxygen. We should expect these bonds to be polar, because holes behave like positive charges. Hence photo-electric emission in the case of quartz can be considered to be similar to that in alkali halide crystal.

One is inclined to believe that the arrangement of the half values of the absorption co-efficient on the short wavelength side for different temperatures at the same wavelength (4900 Å) as well as the fact that the band maxima shift towards longer wavelength are sufficient indication that the coloration arises from a number of identical absorption centres which have the same absorption peaks (Seitz, 1946).

Excitation. The salient features of excitation are the broadening of the absorption band, the decrease in the value of the absorption co-efficient in the band maximum, and the shifting of the band maximum towards longer wavelengths, which phenomenon is markedly found at low temperatures. On the basis of origin of the F-band explained by Gyulai (1925) and Hilch and Pohl (1931), we shall discuss the explanation given regarding this phenomenon. Excitation, according to Gudden and Pohl (1926), is supposed to arise from ejection of electrons by absorbed light. The ejected electron moves through some distance in crystal lattice from the active centre by virtue of the energy received from the absorbed photon. The centres do not remain positively charged on this account. If they were all to become charged, their absorption spectrum would be shifted a considerable distance in the ultraviolet. That such a thing does not happen shows that the centres

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become neutral by taking electrons from the surroundings. This process continues until the centre finds itself strongly influenced by the positive charges in its immediate neighbourhood and is thus capable of absorbing light of longer wavelength than was hitherto possible. This would account for the extension and increase of the absorption in the long-wavelength side of the absorption band. Seitz considered the striking differences of F' band from the F-band. One important fact is that the width of the F' band is relatively insensitive to temperature. He took into consideration the later work of Pick (1938) and of Glaser (1937) regarding the dependence of the displacement range of the photo-electrons on concentration of F centres. He then comes to the conclusion that the F-band arises from a transition between two discrete levels because the F-band represents a transition from a single discrete level to an ionization continuum, on account of the fact that the F-centres can be ionised with all the wavelengths lying in the F' band at all temperatures.

From the nature of the F-and F'-bands it appears that in the case of the F-band, the electrons are attached to the lattices, while in the case of the F'-band the electrons are free to move from lattice to lattice and thus behave like electrons in a conductor, This is all that can be said at present.

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