SPECTROSCOPIC STUDY OF AMETHYST QUARTZ IN THE ULTRAVIOLET AND INFRARED REGIONS*

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Plate XV

ABSTRACT. In this paper a study is made of the absorption of light in the ultraviolet and infrared regions in amethyst quartz. In the ultraviolet the presence of the V-band is masked by the presence of iron impurity and it is difficult to assert its presence. That such a V-band exists was shown by Choong. In the near infrared three absorption bands are observed; the one on the long wavelength side can be identified with the M-band and the others as bands due to impurity. All these facts lead to the conclusion that the factors responsible for colour in the case of coloured alkali halides are also responsible for the coloration of amethyst quartz, with some slight difference.

INTRODUCTION

In a previous paper (Vainu Bappu, 1952) a detailed study was made of the absorption of light in the visible region by amethyst quartz and it was shown that the observed absorption band, the F-band, was similar to the F-band observed by Pohl and his co-workers (1937, 38) in the alkali halides. Along with the study of the F-band in rocksalt, Pohl and his collaborators had subjected another band, observed in the ultra-violet, to intensive investigation. Molnar (quoted by Seitz, 1946) observed that when a crystal of colourless rocksalt was bombarded by X-rays, a band in the ultraviolet called the V-band was formed simultaneously with the F-band. The position of this band in the different alkali halides differed from each other but were all dependent on the lattice constant of the sepcimen under investigation. However, all these bands are always observed in conjuction with F-bands; as the band in the amethyst quartz has been ascribed to F-centres, it is quite logical to expect a V-band in the ultraviolet. Mollow (1935-37) observed an M-band in the long wave length side in the infrared. It appears that the F-and M-bands are associated with the trapped electrons loosened from the halogen or alkali metal ions, while the V-band is related to the holes in the closed shell structure. An attempt is made in this paper to see whether these bands are also present in the amethyst quartz.

EXPERIMENTAL TECHNIQUE

(a) *Ultraviolet.* For absorption in ultraviolet the specimen was held in an aperture in a card board and interposed in the light beam. The

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transmitted light was condensed by means of quartz cylinderical lens on to the slit of the spectrograph. The photographs in Plate XV, figures 3 and 4 revealed a transmission limit of 3800Å for small exposures while for long exposures the limit was extended to 3600 Å. To see if further exposure using a powerful light source would extend the transmission limit, a mercury arc was used and exposures of the order of 45 minutes could just reveal the bright line near 3140 Å.

As complete opacity sets in by about 3800 Å for reasonably moderate exposures, absorption spectra could be photographed easily using a gas filled tungsten lamp with a thin glass bulb. The glass for exposures of one minute absorbed wavelengths shorter than 3100Å transmitting freely in the region upto 3200Å. As such, a bulb of this type run on a higher voltage than usual was used as source for densitometric measurements, which were made in the usual way.

(b) *Infrared.* Studies in the infrared are usually carried out by thermopiles, but as the region of interest in this case was below 10,000Å a photocell sensitive to the red and near infra red regions was used. Though the photocell is quite at a disadvantage for spectral energy measurements, yet in the regions for which it is sensitive a great accuracy can be attained which is limited only by thermal emission and leakage between the electrodes. The measurement of currents greater than 10^{-10} ampere was done by amplifying the photo-current by a D. C. amplifier. This was originally designed by Yu (1946) but in the present amplifying system (figure 1) certain changes were made.
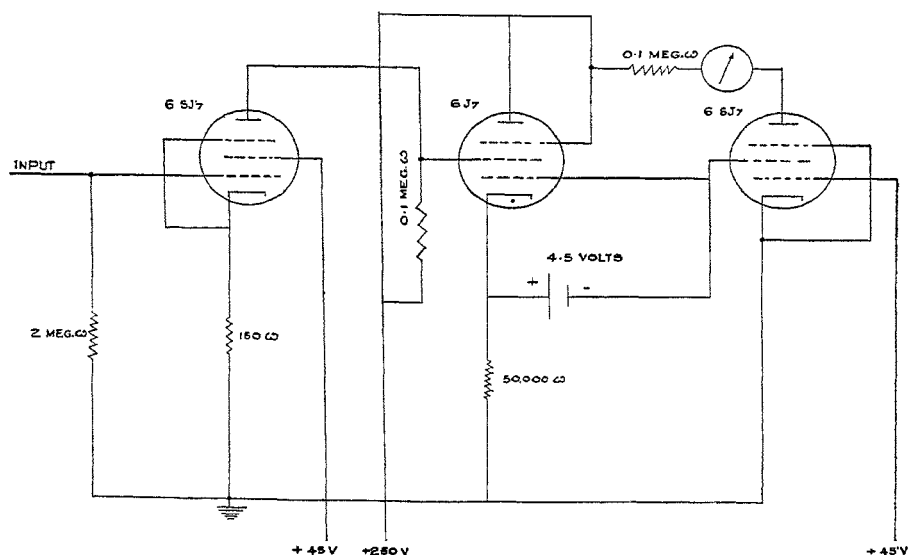

FIG. 1
Circuit diagram of the amplifier

It was found that by introducing the galvanometer in the output of the second valve, a greater steadiness in output valve was obtained. To counteract the steady output current of the valve, an opposing current was passed through the galvanometer which could exactly balance it. But for currents lower than 10^{-10} ampere, a Lindemann electrometer was used.

The source of light was a 150 candle power pointolight lamp, the radiation from which was condensed on to the slit of a spectrometer. A filter was used to cut off all radiations below 5200Å. As the dispersing element was a plane grating, the filter served the purpose of cutting of all radiations less than 5200Å in the second order sepectrum thus enabling values to be obtained oonveniently till 10,000Å in the first order. The specimen was held in a suitable holder and placed in between the filter and the collimator. The radiation from the grating is condensed on to a slit capable of admitting 40 Å at a time in the red region, by means of long-focus achromatic lens. The photo cell was placed in a black housing with an aperture in front containing a narrow slit. The radiation ensuing from the first slit is condensed on to the second, by means of a quartz cylindrical lens. The photocell used had a caesium oxide surface sensitive to radiation between 5000Å and 12000Å. The current was measured by determining the time rate of increase of potential of a small high quality condenser.

$$\text{If} \quad Q = CV$$

$$dQ/dt = i = C\frac{dV}{dt}$$

The capacity of the condenser was adjusted initially so that the time for charging the electrometer to a potential of one volt was between 10 and 35 seconds. The value finally adopted was 250 micro-micro farads. The absorption coefficients were determined by noting the times of charging the electrometer needle to potential of one volt, with and without the specimen before the slit of the instrument. As the times of charging are inversely proportional to the intensities of incident light the quantity η which is the transmitted fraction of the incident energy becomes equal to

$$\eta = \frac{I_2}{I_1} = \frac{t_1}{t_2}$$

were I_2 is the transmitted energy, I_1 the incident energy. and t_1 and t_2 being the times of charging the electrometer with and without the sepecimen, the mean of eight readings being finally abopted.

Figure 2 shows in detail, the arrangement of the infrared monochromator as well as the Lindemann electrometer.

The complete spectrometer was first calibrated for the mecury radiations 5461Å and 5780Å as well as D_1 and D_2 lines of sodium. As the voltage of the cell was quite low the photoelectric responses for different intensities were quite linear.
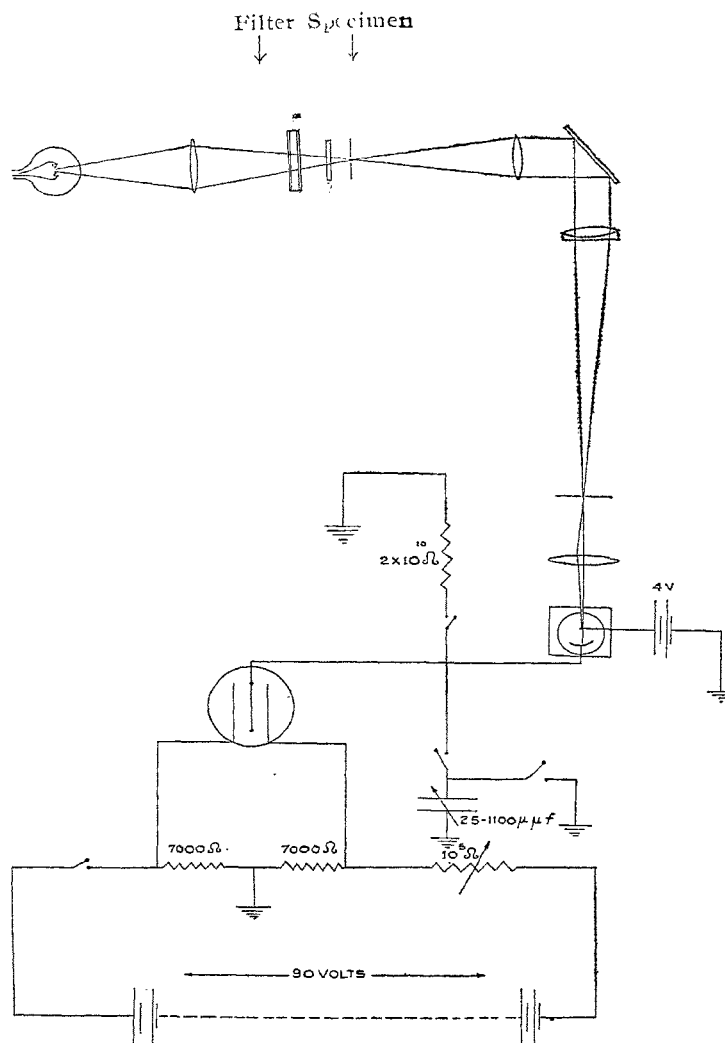
Filter Specimen

FIG. 2

Infrared monochromator together with the Lindemann electrometer and photocell

Much of the work was done in the winter months when the atmosphere was dry. As an additional precaution all work done with the electrometer was on sunny days with perfectly clear skies when reading could be reproduced properly.

For detecting the M band specimen, A_1 was used while the decolorised specimen A_2 was used to show which of the bands observed are due to impurities and which are not.

RESULTS AND DISCUSSION

Table I below gives the density values and corresponding absorption coefficients for different wavelengths. These can be seen diagramatically represented in figure 6. An absorption band reaching opacity by 3000Å

PLATE XV

Fig. 3

Transmission limits of amethyst quartz in the ultraviolet, (specimen A_1), for different exposure times

(a) 1 minute, *(b)* 3 minutes, *(c)* 7 minutes, *(d)* 15 minutes
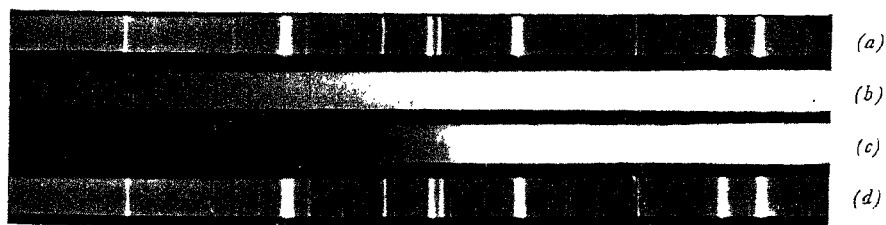

Fig. 4

Absorption spectrum of amethyst quartz in the ultraviolet

(a, d) Hg arc comparison spectrum

(b) Decolorised specimen A_2

(c) Specimen A_1

can be seen to be present. This band occupies just the same position and shape which a V-band in rocksalt does. To test whether this band is really a V-band, we have to resort to heat treatment.

TABLE I

Absorption coefficients for amethyst quartz in the ultraviolet

Wavelength in Angstrom units	Density	Absorption coefficient per cm
4046	0.077	10.93
3875	0.457	23.47
3620	0.591	30.10

The sepecimen used for the study of the removal of F centres by thermal treatment was used for absorption in the ultraviolet. No radical change in the transmission was noted after the heat treatment, even after removal of all the F centres. Consequently, we have to infer that the band in the ultraviolet in amethyst quartz is not a V band but it may be some band which masks entirely the effect of the V-centres, if any such exists.

In Plate XV, figure 4, we have the absorption in the visible and ultraviolet regions of both the specimens A_1 and A_2. Specimen A_2 has a greater transmission in the ultraviolet than the specimen A_1. But this was just the case before decoloration, and hence the increase in the transmission cannot be ascribed to thermal treatment. Plate XV-figure 3, shows the transmission limits in the ultraviolet for specimen A_1 for different exposures. For very long exposures the limit does not exceed 4630Å.

Koch and others have noticed that small quantities of thallium halides may be dissolved in the alkali halides and that the resultant mixed crystals exhibit narrow absorption bands in the ultraviolet, visible and near infrared regions. As many previous investigators have detected iron in the form of Fe_2O_3 in amethyst quartz, it is quite possible that the band in the ultraviolet is due to the presence of iron as impurity. Unaffected by thermal treatment, the band in the ultraviolet remains as it is, in spite of removal of F-centres [Plate XV, figure 4(b)]. Further, in the absorption spectra of specimens A_1 and A_2 we find different transmission limits, the limit in the case of A_2 being about 3300Å for short exposures while that of A_1 is in the neighbourhood of 3800Å. Thus we see that transmission limits do fluctuate from specimen to specimen. This can be explained as due to the difference in iron content of the two specimens. And this is all the more probable because specimen A_2 was picked up from a different quarry.

The absorption curve for coloured amethyst quartz indicating the different bands in the infrared can be seen in figure 5. For coloured amethyst quartz we have three distinct bands with maxima at wavelengths

7850Å, 8350Å and 9200Å respectively. The bands at 7850Å and 8350Å are bell shaped and fairly narrow, whereas, that with maxima at 9200Å is very broad as can be seen clearly in curve(A) of figure 5. In the decolorised specimen we have two bands at 8350Å and 9200Å respectively, the positions and respective shapes being identical with the two bands in the coloured variety. The band at 7850Å is completely missing in decolorised specimen A_2, while the 8350Å band of A_2 has a higher absorption than the corresponding one in A_1. But there is a decrease in the magnitude of the 9200Å band of A_2 when compared with A_1.
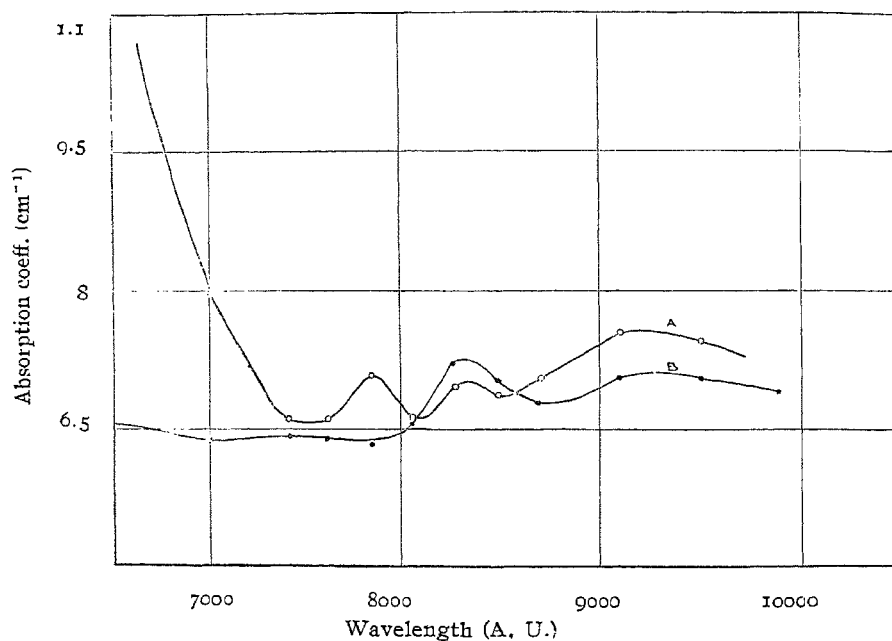

FIG. 5

The absorption curve of amethyst quartz in the near infrared.
A. Amethyst quartz specimen
B. Decolorised amethyst quartz

The 7850Å band is thus removed completely by thermal treatment, whereas, the other bands are not. Therefore, its origin is akin to that F-band. It can, therefore, be an R-band or an M-band. R-bands are usually found on the long wavelength foot while M bands are situated farther on, on the normal absorption curve. As the 7850Å band is slightly away from the long wavelength foot it may be considered to be an M-band.

Of the two other bands we find that thermal treatment has no effect on their structure. As such it cannot be due to any absorption centres of the type of F-and M-centres. And as we have an impurity band in the ultraviolet, it is quite probable that these may owe their origin to such impurities, in this case the impurity being iron.

CONCLUSION

In figure 6 is given the complete absorption curve of amethyst quartz in the ultraviolet, visible and near infra-red regions, showing the F-bands, and M-bands and a band in the ultraviolet. The curve is almost similar to the one obtained by Molar in the case of potassium chloride irradated by X-rays except for the band in the ultraviolet which may perhaps be due the iron impurity. Choong (1945) has, however, obtained a band in the ultraviolet in the case of fused quartz coloured violet by radium rays. The slight humps beyond the F and M bands may also be due to the impurity as these appear also in the infrared spectrum of the bleached crystal.
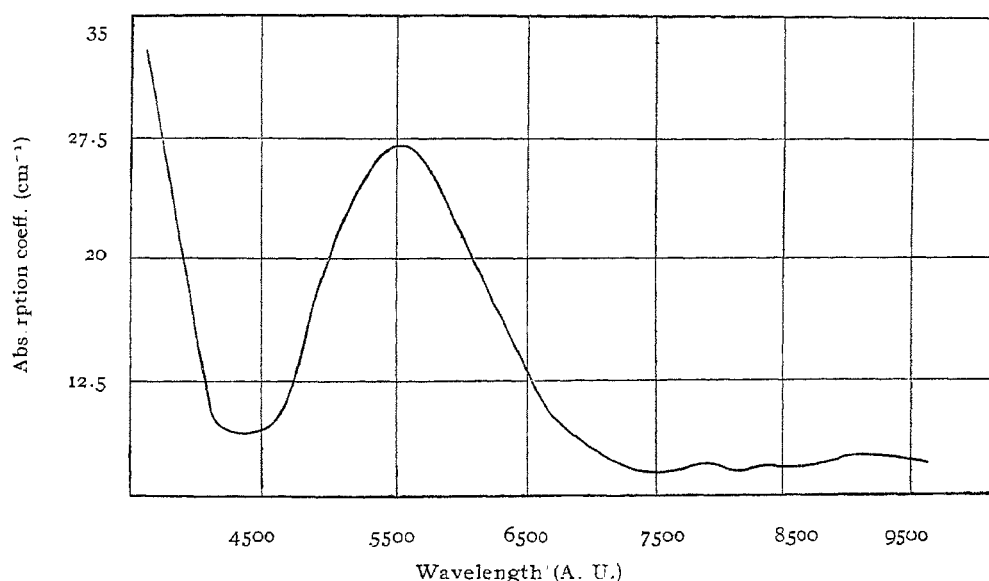

FIG. 6

Absorption curve of amethyst quartz in the ultraviolet, visible and near infrared regions

Seitz is of the view that a centre formed by combining an F-centre and a pair of vacancies may be responsible for the M-band. That the whole absorption phenomenon observed in the case of amethyst quartz is almost similar to those observed in coloured alkali halides, shows that the process responsible in both cases must be of same nature. These facts also establish that amethyst quartz behaves like a polar crystal, as far as absorption is concerned. This receives further support from the study of the photo-conductivity. Finally, it can be said with confidence that the colour of amethyst quartz is due to the colour centres formed by exposure to penetrating irradiation at some remote period in the evolution of the earth.

ACKNOWLEDGMENT

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