ON THE PHOTOCONDUCTIVITY OF AMETHYST QUARTZ*

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ABSTRACT. This paper describes an investigation of the photoconducting nature of amethyst quartz. Measurements of photocurrent were made for varying voltages, intensities, radiations and temperatures. A spectral sensitivity curve of photoconductivity duplicates the optical absorption in the visual region identified as the F-band. The photocurrent is found to be proportional to light intensity and voltage; in the latter case secondary currents deviate the relationship from strict linearity. Under constant irradiation of light in the maximum of the F-band, the crystal is shown to be "excited". Lastly, measurements of photocurrent at different temperatures under radiation sources that yield both the electron primary current and the positive primary current, show that the curves obtained are identical with those obtained by Pohl and collaborators in the case of coloured rocksalt. The similarity of the behaviour of amethyst quartz and coloured rocksalt is so very striking that it seems very reasonable to ascribe the colouring of amethyst quartz to F-centres caused by high frequency radiations.

INTRODUCTION

Systematic studies of the photoconductivity of crystals have shown that we can classify them into two categories. Idiochromatic crystals are those whose photoelectric properties are determined by the material itself and not by any naturally present or artificially introduced impurities. Allochromatic crystals on the other hand are inactive photoelectrically in the pure state, but active when foreign atoms or particles are dispersed through their volume. The naturally and artificially coloured alkali halides, studied extensively by Gudden, Pohl and collaborators in Germany fall into this latter class.

The differences between allochromatic and idiochromatic crystals become readily apparent when one studies their absorption spectra and their photoconducting nature. In idiochromatic crystals the photoelectric current is directly proportional to the incident light quanta and increases as we go to the ultraviolet, until a high rate of recombination is reached in the crystal. In allochromatic crystals, where F-centres are responsible for the colour as well as the enhanced electrical conductivity under the influence of light, the spectral response curve of photoconductivity follows closely the F-band. The "excited" spectral response also duplicates closely the trend indicated by the F-band.

In an earlier investigation the author (Bappu, 1952) has shown from a study of the absorption spectrum in the visible region that amethyst quartz may be considered as essentially an allochromatic crystal. The absorption in the

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ultraviolet and near infrared regions (Bappu, 1953) also confirms this hypothesis and reveals the slight deviations present from the identical behaviour of an alkali halide crystal exposed to high frequency radiation. In what follows, we shall report on a study of the photoconductivity of amethyst quartz and show conclusively that its colour is acquired in a fashion similar to that of an allochromatic crystal.

EXPERIMENTAL

The conductivity was measured by the well known Curie method with the aid of a Lindemann electrometer. The electrodes used were crocodile clips and the springs in them had sufficient tension to ensure a good contact between the specimen and electrodes. An earthed copper guard ring prevented any possible surface leakage. The current was measured by noting the charging rate of a precision high quality condenser. The value of the condenser used for measuring very low currents was 94 $\mu\mu$f while for appreciable currents, of the order of 10^{-12} amperes, a value of 110 $\mu\mu$f was employed. The high tension source for values less than 180 volts was a set of dry batteries, the output of which for all purposes may be taken as constant over the period. For voltages greater than 180 volts, a rectifier capable of giving potentials up to 500 volts was used.

The source of light employed for exciting the F-centres was a 250 watt tungsten filament lamp run on A. C. voltage; the light from this lamp was focused on to the entire area of the specimen between the electrodes. Three spectral regions with effective wavelengths of 5500 Å, 4600 Å and 5900 Å and having bandwidths of about 500 Å were isolated by means of filters. Light from a 150 C. P. pointolite lamp, after passing through a red filter, acted as the source of long wavelength radiation. In the study of the variation of photocurrent with light intensity, the relative intensities were deduced by applying the inverse square law.

For maintaining the specimen at a temperature higher than that of the surroundings, a heater provided with two mica windows as entrances for the exciting light and red light was used. Measurements were made only when steady temperatures were attained and maintained for at least half an hour, as indicated by a thermometer placed virtually in contact with the specimen.

RESULTS

(*a*) *Dependence of photocurrent on light intensity and applied voltage.* One of the most significant features of the primary photoelectric current that has been observed in every photoconducting crystal, is the strict proportionality between the current and the intensity of the exciting light. Secondary currents do bring in their own complications to upset this rigorous proportionality, as will be seen in the intensity curve of molybdenite, obtained by Coblentz and collaborators and reproduced by

Nix (1932). In the case of the variation of primary current with voltage, we get curves showing saturation for fairly high values of electric field. Saturation could be attained fairly easily in idiochromatic crystals, while in allochromatic crystals they can be found only with great difficulty.

To determine the variation with intensity in the case of amethyst quartz, a current obtained fifteen seconds after illumination had started, was utilized. The variation was studied with two different radiations, green and yellow. The current obtained was strictly proportional to the intensity of the light. As can be seen in figure 1, both the curves are parallel to each other showing that the difference in value of photocurrent was caused by a difference in absorption.

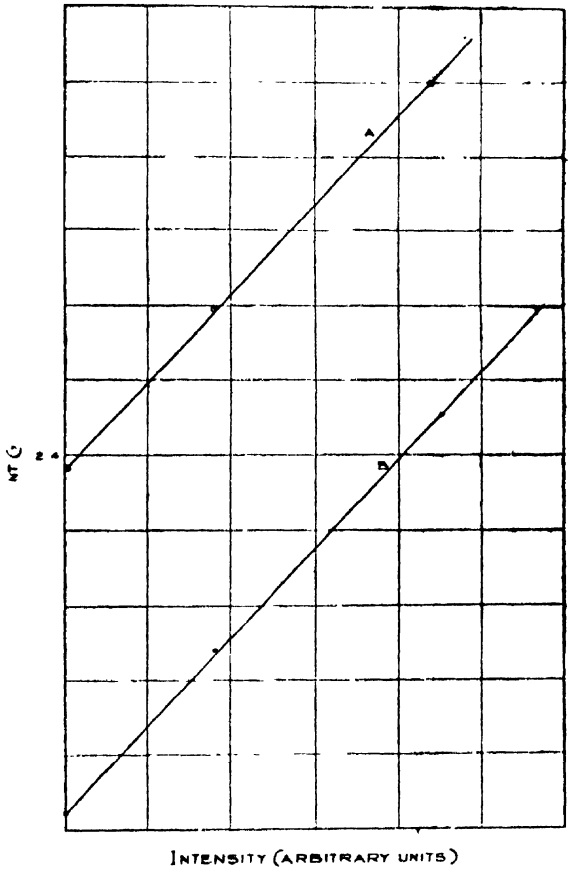

FIG. 1

Variation of photoelectric current with light intensity
A. Green light. B. Yellow light

To test the dependence on voltage, readings were taken one minute after the beginning of illumination in the blue and green regions of the spectrum. These measurements were taken in a way that facilitated the indication of the presence of secondary currents. No tendency for saturation occurred

as can be seen in figure 2. On the contrary the current increased considerably with higher voltages, thus indicating the major share taken up by secondary currents.

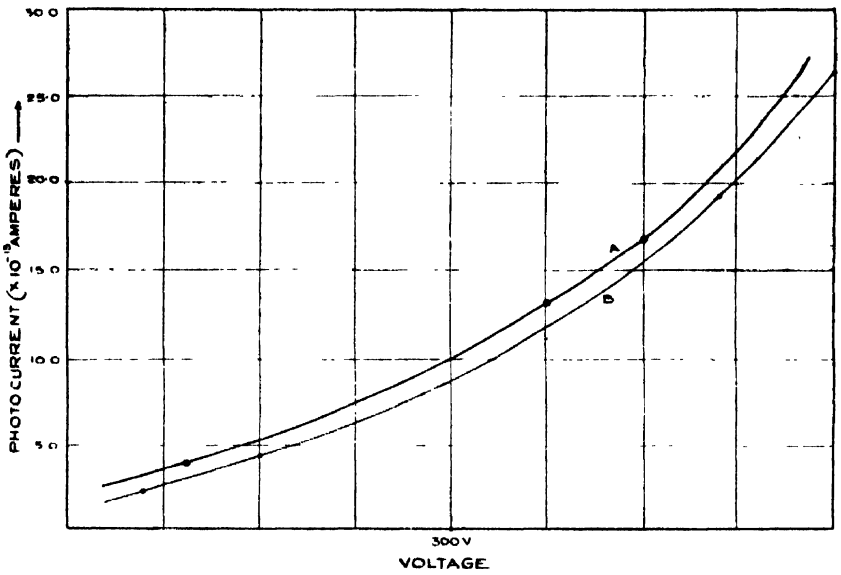

FIG. 2

Variation of photocurrent with applied voltage
A. Green light B. Blue light

(*b*) *Photoelectric responses for different wavelengths*: For investigating spectral sensitivity it is essential that the spectral regions isolated from a light source by filters or by a monochromator should have the same spectral energy. In the following experiments accurate spectral energy measurements could not be made and so the different spectral regions could not be equalised with respect to their energy contents. However, by combining the energy distribution of the tungesten lamp with the transmission data of the filters, the assumption that for all practical purposes the relative transmitted energies of the three filters are equal, seems valid. The measurements of the initial jumps of the primary current are used to obtain an idea of the degree of excitation, produced by the different radiations, of the F-centres.

Figure 3 demonstrates the photoelectric responses of a specimen of amethyst quartz to green, blue and yellow light and also to white light. The measurements being green, blue and yellow exciting radiations constitute a continuous run, the crystal being irradiated with red light at the end of each dark period that follows one of excitation. Let us consider first the effect of green light alone. Instantly on illumination we have a sudden rise of 1.2×10^{-13} amperes in the value of the current. This is the primary current. If at this stage the primary current had continued steadily, the current curve would have been parallel to the time axis. But

instead we find a slow but regular increase in the value of current showing that with time the resistivity of the crystal has decreased. This current is the secondary current because it has developed here with the aid of the primary current and with a time lag. Intense lighting, together with imperfections are responsible for the formation of secondary currents. Hence in crystals with twinnings, some glasses, and tablets of compressed powders the primary photoelectric current is largely suppressed and only a high secondary current is observed. In view of this fact it is not surprising, if in amethyst quartz, the lattices of which are distorted by the presence of metallic impurity, a secondary current manifests itself.

The decrease in value of current at the fifth minute after illumination is due to the formation of a space charge which tends to nullify the regular inflowing current. The mechanism of the secondary current can be considered as follows: When the crystal is irradiated with light in the F-band, photoelectrons are released, and under the influence of the electric field they move towards the anode. A large or small number of photoelectrons is released depending on the absorbed energy and we get correspondingly a large or small primary current. The continued passage of the primary current appears to break down the resistance of the crystal, so that electrons can enter the crystal from the cathode and pass to the anode. When the primary current flows, a few of the photoelectrons are trapped at impurity centres or at surfaces of discontinuity, forming channels as a results of which the effective resistance of the crystal decreases. This current constitutes the secondary current. Due to the flow of the photoelectrons, a positive charge builds up in the crystal and tends to annual the incoming electron flow. This accounts for the decrease in current after the fifth minute. A few of the incoming electrons neutralise the positive charges behind, while further positive charges are formed continuously due to the drift of the photoelectrons under the influence of light. The saturation value is obtained when a number of electrons coming in from the cathode neutralises the positive charges, the current being observed due to the motion of the photoelectrons. At the eighth minute when the light has been turned off there are no more photoelectrons released and a sudden fall in the current is noticed, showing that the photoelectrons do not contribute anymore to to the current. After this sudden drop the current decays with a time lag until the normal value of the dark current is reached, because the conducting channels lose the electrons of which they are made.

In the case of the photoelectric response with blue light we find an initial jump of 09.5×10^{-13} amperes constituting the primary current. The development of the secondary current can be noticed, but there is again a space charge formed which decreases the current. The absence of a sudden fall immediately on turning off the light, indicates, that the incoming flow of electrons just neutralises the positive charges released.

With yellow light we have a rise of 0.85×10^{-13} amperes constituting

the primary current. The secondary current formed, keeps increasing without any space charge being formed, showing, that the positive charges are being nullified by the electron flow from the cathode. The conducting channels decay rather rapidly to restore normal conditions once again.

Comparing the initial jumps in values of the current, under the influence of green, blue and yellow radiations we find that the green radiations have a greater effect in producing photoelectrons than the blue and yellow regions of the spectrum. This indicates that the photoelectric spectral distribution curve has a maximum in the green region, with blue and yellow having lower values, thus forming a bell shaped curve similar in shape to that of optical absorption. This behaviour is just as expected, for amethyst quartz has been proved optically to be essentially an allochromatric crystal.

The above measurements were repeated after 24 hours, so that the crystal may revert to its original condition. The full radiation of the lamp was turned on, as the source of white light. A different electrode spacing gave a slightly higher field, which in turn accounts for a slight increase in value of the dark current. The variation in current under the influence of white light, as seen in figure 3, shows that the difference between the final value of the current and the dark current is more than twice that in the case of green light. As white light consists of radiations both on the short wavelength and on the long wevelength side of the F-band, we can assume that a large number of photoelectrons is created and conduction channels are formed, while the locations of the positive charges formed are made mobile by the long wavelength radiations of the red and infrared regions. As secondary currents depend on primary currents for their formation, which in turn depend on the exciting wavelength, we have indirectly a relation between the magnitudes of the secondary currents and the respective wavelengths responsible for their creation. This can be found in the case of molybdenite where the secondary currents due to $\lambda 9900$ are about eight fold greater than those due to $\lambda 24100$. In ameythyst quartz, we have the secondary current assuming large proportions because of the sum total of the roles is played by all the diffrent wavelengths. The rapid decay in darkness shows that under the influence of long wavelength light most of the locations of positive charges had slipped to the cathode. It is because of the simultaneous flow of the positive primary current along with the ordinary flow that the final value of the current in the case of white light is more than double that in the case of green light. The definite time lag present in the decay after illumination with white light illustrates that conduction channels play an appreciable part.

(*c*). *Excitation in amethyst quartz*: Rontgen and Joffe (1921) found that the spectral sensitivity of coloured rocksalt by X-rays was influenced by the order in which measurements are made. Later investigations on rocksalt have shown that the crystal when excited yields a spectral sensitivity

curve which has a maximum of lower value than in the unexcited condition. In amethyst quartz, excitation and effect of current flow were observed together and are shown diagramatically in figure 4. The crystal was irradiated and kept in darkness, measurements being taken in the meanwhile. Two more runs of this type were made without giving any time for the crystal to come back to normal condition.

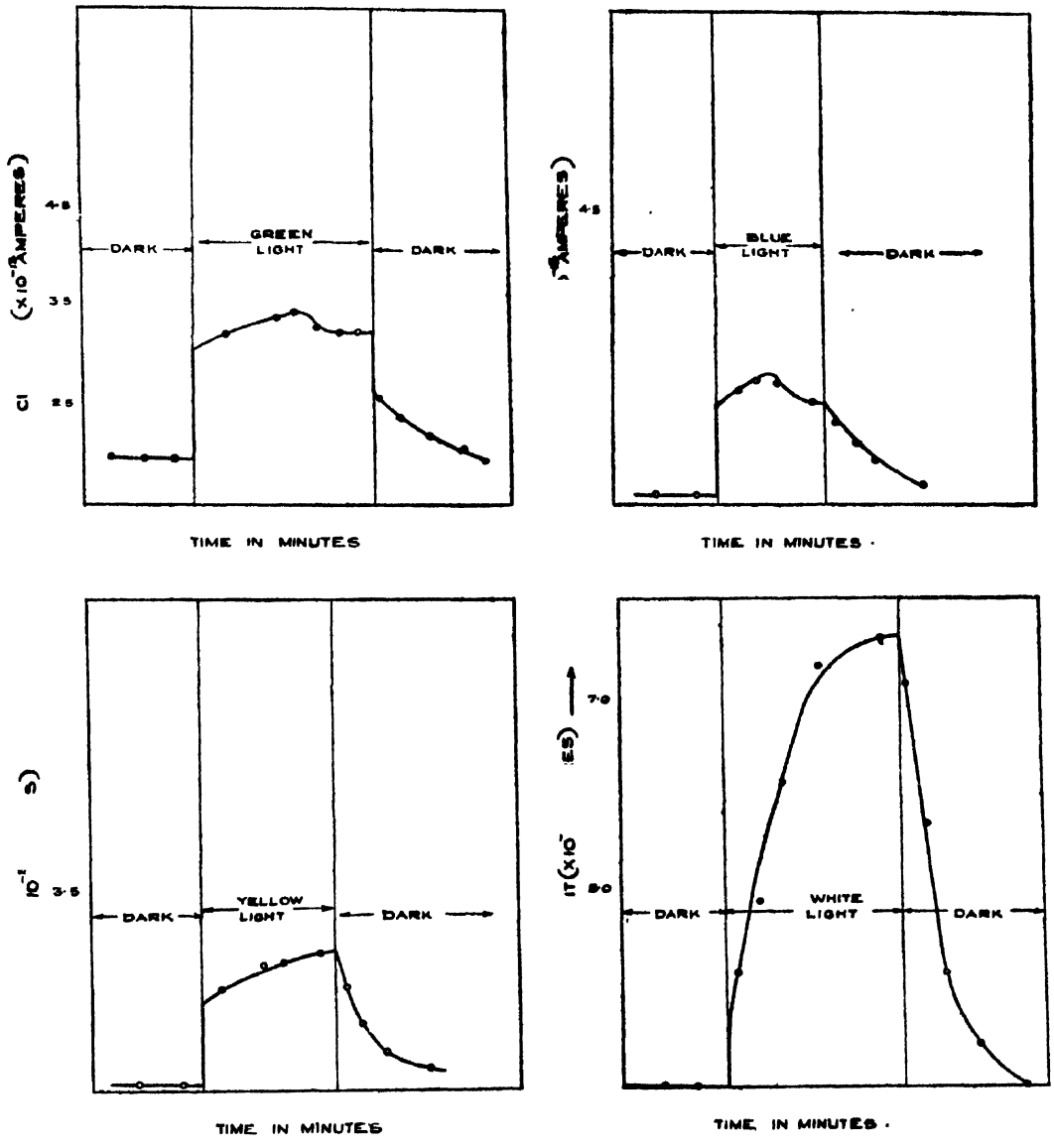

FIG. 3

Photoelectric response *vs* time of illumination

A comparison of diagrams (*a*), (*b*) and (*c*) will show the changes that have taken place. The transition from digram (*a*) to (*c*) indicates a decrease

in dark current of 0.25×10^{-13} amperes. This decrease can be ascribed to polarisation which is so often found in insulators of the type of quartz.

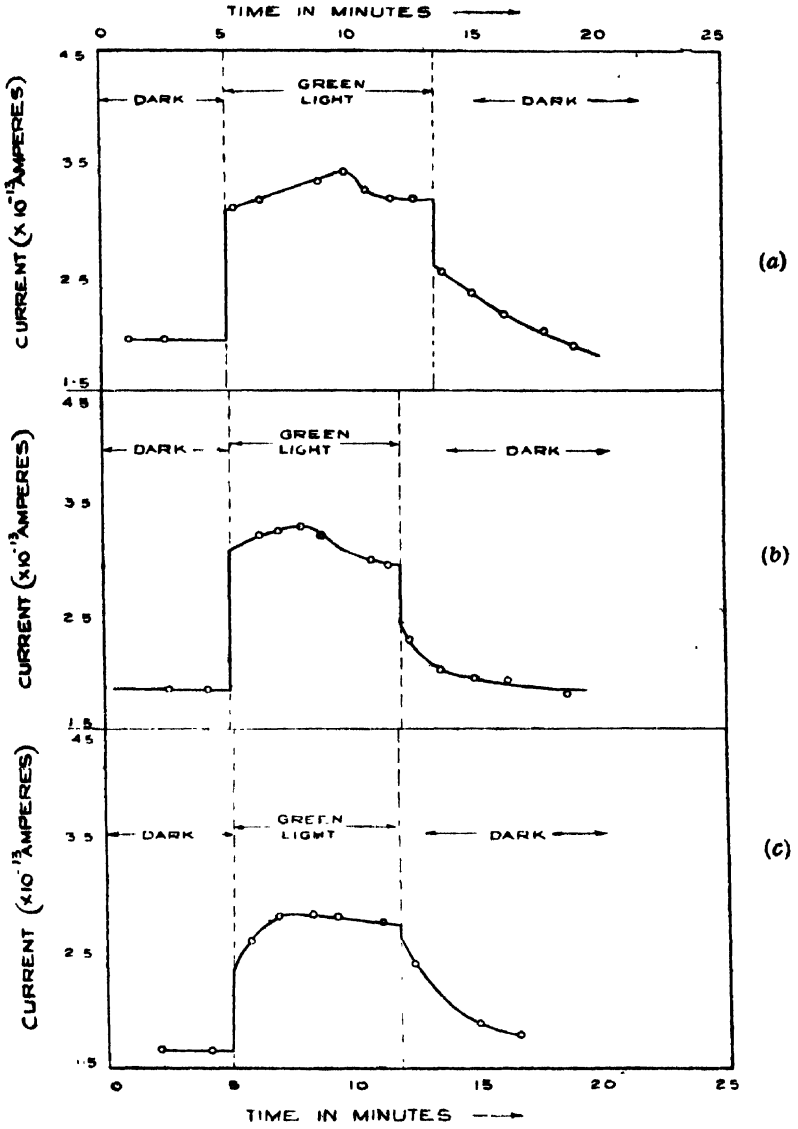

FIG. 4
Excitation in amethyst quartz

On illumination we find in case (*a*) a primary current of 1.2×10^{-13} amperes as against one of 0.65×10^{-13} amperes in case (*c*). Also on the termination of illumination the fall in the first run is 0.53×10^{-13} amperes and 0.2×10^{-13} amperes in the third case. The difference between the fall in current in the first and second runs is not as striking as in the case of the first and third. Such a behaviour is due to the different periods of illumination in the two cases and hence if in the second run the crystal was bathed for a greater duration with green radiation, the magnitude of the

fall in current when the light intensity is turned off would have been much less than observed. The decrease in values of the primary currents from (*a*) to (*c*) is a clear and definite illustration of 'excitation" in amethyst quartz.

(*d*). *Photoelectric currents at different temperatures:* Gudden and Pohl have studied exhaustively the photocurrents obtained at different temperatures in the case of yellow sodium chloride. Figure 16 of Pohl's survey article (1937) gives a diagrammatic representation of the data obtained at four different temperatures. In figure 5 the results obtained in the case of amethyst quartz for the temperatures 33°C, 90°C and 128°C can be seen. The procedure followed was exactly that adopted in the case of sodium chloride. After a dark interval the crystal was exposed to green light (corresponding to the F-band), followed by an interval of darkness. Lastly, the crystal was flooded with red light. A voltage of 90 volts was applied, the distance between the electrodes being 0.7 cms.

At room temperature a primary photocurrent of 0.1×10^{-13} amperes was obtained. Such a value does not seem high when compared with previous measures, but in view of the fact that the experiment was carried out with a smaller value of the electric field and a lower light intensity, this jump is not too low. The current increased with time upto the fifth minute after illumination, and reached a saturation value of 2.6×10^{-13} amperes. At the end of the eighth minute after illumination the light was turned off. A drop in value of 0.4×10^{-13} amperes occured, followed by a decay to 1.9×10^{-13} amperes in current value, was noticed. This decays quickly at first and slowly afterwards with time, reaching the dark current value obtained before the experiment was performed.

At 90°C the dark current was 8.75×10^{-13} amperes. Instantly on illumination, a primary current of 6.25×10^{-13} amperes was noted. A steady increase in current value could be seen, but it was not much when compared with the increase at 33°C. A drop in value of 1.0×10^{-13} amperes occurred when the illumination terminated. After four minutes of darkness an instantaneous rise in value of 1.5×10^{-13} amperes was noted with the red source on, followed by a current decay back to the initial value.

The dark current at 128°C was 14.5×10^{-13} amperes. An observation made half a minute after the beginning of illumination revealed an increase of 17.0×10^{-13} amperes. But even when the green light was on there existed a steady decay in the behaviour of the current. The decay continued still further in darkness. On turning the source of red radiation on, an increase of 3.5×10^{-13} amperes was noted.

At 33°C the fall in value of current immediately on turning off the green light source is nearly four times the initial jump. A possible explanation of this can be given as follows. A few of the electrons are trapped. Due to the electron flow by virtue of the primary current these are released temporarily and some of them get trapped once more in vacancies or with

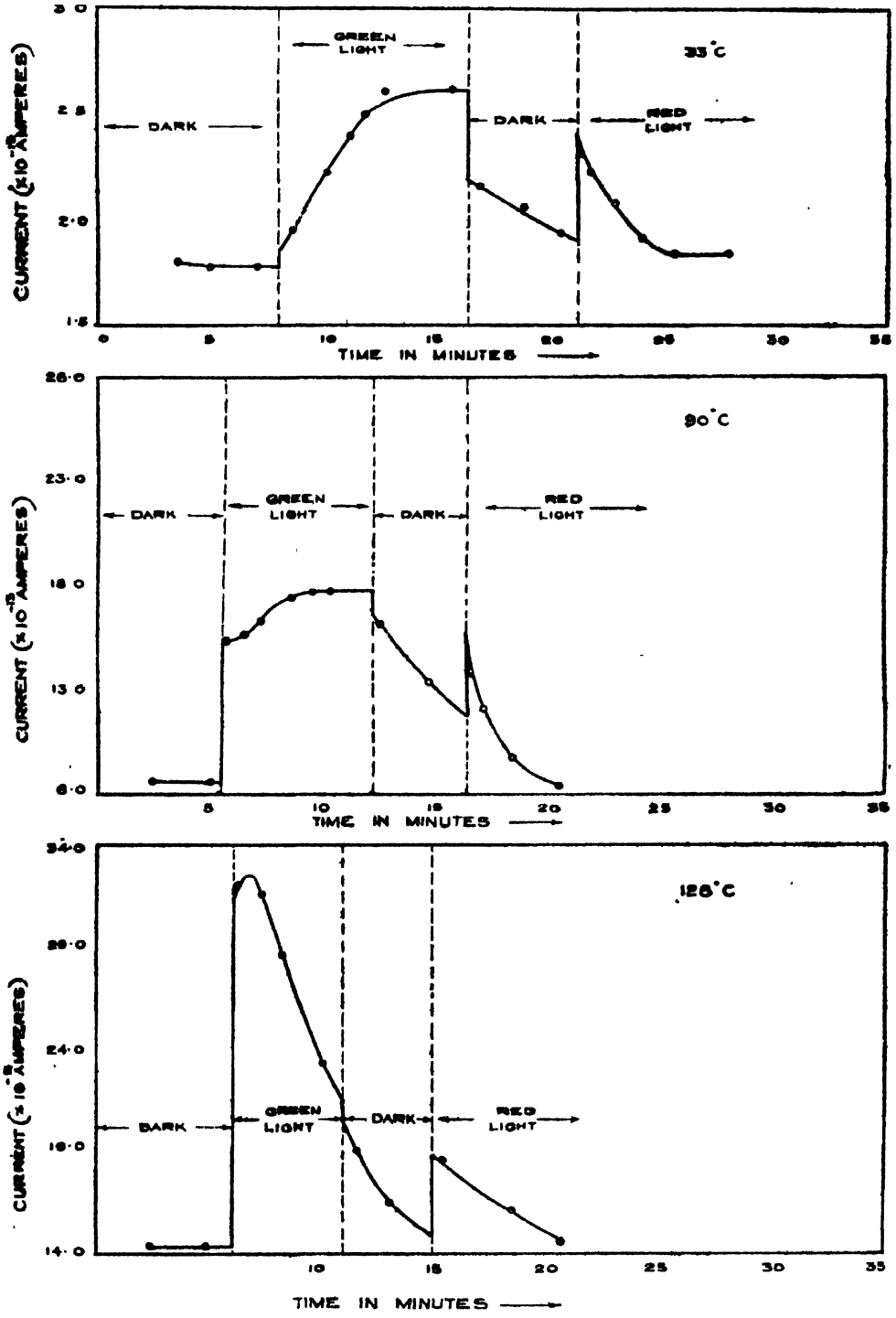

FIG. 5

Variation of photocurrent with temperature

interstitial ions. The green light releases them and they again move a certain distance. Consequently, the number of electrons moving under the influence of light now is greater than initially and hence when the light is turned off a greater fall in value of current is observed. During the dark period the conduction channels formed, decay. The location of a few positive charges slip back to the cathode, thus causing a slight flow of the positive primary current in darkness also. On illumination with red light the positive charges are neutralised completely, as shown by the increased value of the current.

At 90°C a very high jump in value of current, immediately on illumination, is noticed. This is because, simultaneously with the electron primary current, a little of the positive primary current flows as a result of the thermal energy being able to move the electrons further. As most of the positive primary current flows during illumination with green light as well as when the crystal is in darkness, we have a rise in value of current under the influence of red light equal to only two thirds the value of the initial jump on illumination.

The behaviour at 128°C is just a magnification of that at 90°C. But now as a result of the high value of current flowing by virtue of the negative and positive primary currents, the current decreases due to an increasing polarisation which effects the drift of the electrons. A low dark current is observed and the flow of the positive primary current under the influence of red light is very little.

A comparison of the three curves indicating behaviour under the influence of red light will show that with time, at room temperature the current decay is quick initially and slow later. At 90°C it decays fairly quickly while at 128°C it varies linearly with time. This difference is due to the increased mobility of the locations of positive charges at high temperatures.

Thus the phenomena of spectral sensitivity, excitation and variation of photocurrent with temperature, exhibited by yellow sodium chloride, are duplicated essentially by amethyst quartz. Along with the optical studies, this investigation indicates rather definitely that amethyst quartz possesses its colour as a result of the presence of F-centres, formed possibly by high frequency radiation.

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