

Light Emission Produced by Current Injected into a Green Silicon-Carbide Crystal*

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This paper deals with the light emission, which arises from the passage of a current in the forward direction over a p - n -barrier in a transparent ("pure") silicon-carbide crystal. The results differ from previous results obtained on a dark blue (impure) silicon carbide crystal in several respects: The spectral distribution of light emission is found to be independent of current and temperature. Both the efficiency of light emission and the decay constant of light emission increase exponentially with decreasing temperature. This is explained by a nonradiative transition of excited electrons. In a dark blue (impure) silicon carbide crystal, the resistances in series with the p - n -barrier were largely eliminated, and light emission at a voltage of the same magnitude as $h\nu/e$, was observed.

1. INTRODUCTION

IN a previous paper, investigation of the light emission from blue SiC crystals excited by current flow was discussed.¹ The body of the crystals was of the p -type with occasional n -type surface layers.

Since the absorption edge of the SiC lattice lies at about 0.42 microns,² pure SiC should be colorless. The dark blue color of the crystals is indicative of lattice defects or high impurity content. The latter conclusion has now been confirmed by spectroscopic analysis (Table I). It is known that the spectral distribution, temperature dependence, and efficiency of light emission from phosphors depend on the impurity centers (activators, killers) present (e.g., in ZnS, Cu, and Ni, respectively). It is expected, therefore, that there should be differences in the injected light emission from SiC crystals which differ in impurity content. Pale greenish transparent SiC crystals have been obtained through the courtesy of Carborundum Company, Niagara Falls, New York. Such crystals are known to be of the n -type.³ Spectroscopic analysis showed that they are of considerable purity, containing only traces of Al, Fe, Ti, Cu, and Mg. Four of the crystals emitted light with current passing. In this paper, experimental data will be presented on the light emission from one of these green SiC crystals. The intensity of the light emission as a function of current density, temperature, and wavelength was investigated. The response time of

light emission to a current pulse was also measured. The technique is the same as reported previously.¹

2. DESCRIPTION OF THE CRYSTAL INVESTIGATED

The crystal under investigation was wedge shaped. An area contact was made on the base of the crystal. A well-defined area of about 1 mm² on one side of the crystal near the apex was found to emit green light when a current was passed through a catswhisker placed within this area (catswhisker negative).

Probe measurements were made to determine the potential distribution in the crystals. The potential distribution was very complex and indicated the presence of at least two barriers within the crystal. It was established that the boundaries of the green light emitting area coincide with a barrier, and that the green light appears when current passes the barrier in the forward direction.

It has been reported,⁴ that SiC crystals which are phosphorescent under ultraviolet light also emit light when excited by current. We have found this technique helpful in selecting light emitting crystals. It should be noticed, however, that in the case of the crystal under discussion, the area which emits green light when current passes could not be distinguished by phosphorescence under ultraviolet from other parts of the crystal.

If the polarity of current was reversed (catswhisker positive), a yellow light emission with diffuse boundaries appeared. At higher voltages, a bright bluish-white light was superimposed at a few distinct spots.

The area emitting yellow light did not coincide with that emitting green light. Microscopic inspection indicated that each light came from a different depth in the crystal. It seems possible that the two types of light emissions are due to injection of carriers over two different barriers. The difference in color of the emitted light cannot be attributed to the different thicknesses that the light has to pass in order to reach the surface. In the locality of the light emission the crystal was about 1 mm thick. If absorption was an important factor, one would expect the intensity to be markedly

TABLE I. Spectroscopic analysis of a blue SiC crystal.

Al	0.1	Wt percent
Fe	0.05	Wt percent
Ti	0.002	Wt percent
Cu	Traces	
Mg	Traces	

* Most of the data included in this paper were presented at the American Physical Society Meeting in New York, January 31, 1952, paper SC5.

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¹ Lehovc, Accardo, and Jamgochian, *Phys. Rev.* **83**, 603 (1951).

² O. Weigel, *Nachr. Ges. Wiss. Göttingen*, p. 264 (1915).

³ G. Busch and H. Labhard, *Helv. Phys. Acta* **19**, 463 (1946).

⁴ T. Tetzner, *Z. angew. Phys.* **1**, 153 (1948).

different when measured from each side of the wedge since the light had to pass through different thicknesses to reach each surface. The green and yellow light emissions were visible with about equal intensities both from the contact side of the crystal and the side opposite. It seems, therefore, that the different colors observed are to be ascribed to various activator (impurity) centers rather than to absorption.

The bright bluish-white spots which appear when the catwhisker is positive are located at the boundary of the area emitting green light at negative polarity of the catwhisker. These spots appear, therefore, when the current passes the barrier in the blocking direction. The current-voltage characteristic in the blocking direction showed a sharp break which corresponded to the initiation of the blue light spots. The current increased more rapidly with voltage after the break. It is suggested that the light spots arise from recombination of electron-hole pairs which have been created in the barrier by either a Zener effect or by ionization from electron collisions.

Parts of the crystal were found to phosphoresce under ultraviolet light. The color of the phosphorescence was reddish-yellow and about the same color as that of light emission caused by current flow with the point contact positive. A well-defined area of the crystal which included the area emitting yellow light under current flow was phosphorescent. There is one striking difference between the yellow phosphorescence and the yellow light emission under current flow, however. The yellow light emission under current flow decays instantaneously to the eye after interruption of current, whereas the phosphorescence decays gradually within several seconds after removal of the exciting ultraviolet light.

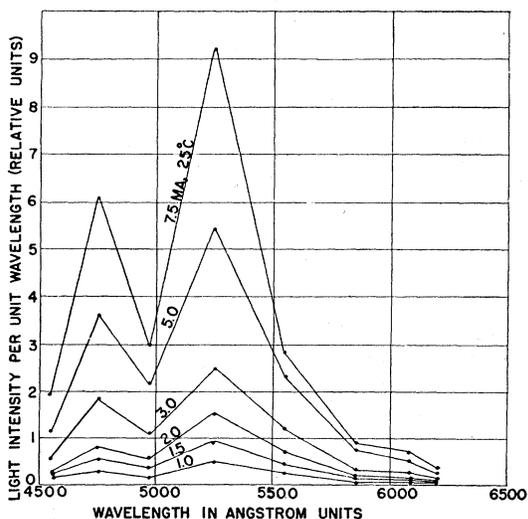


FIG. 1. Spectral distribution of the light emitted from a pale green SiC crystal as a function of the current passed through the crystal at room temperature.

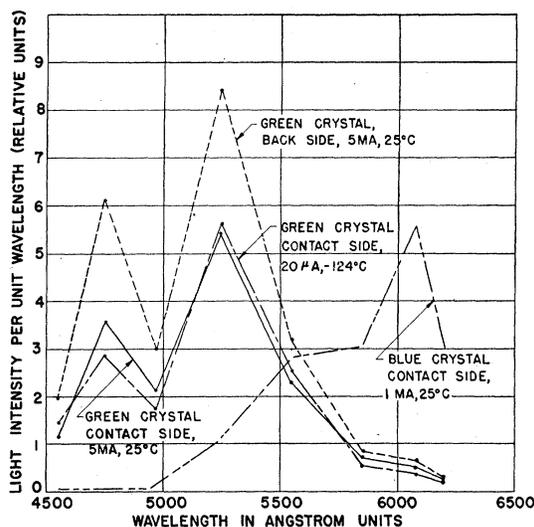


FIG. 2. Spectral distribution curves of the injected light emission from a pale green crystal taken from different sides of the crystal at the temperatures indicated. A spectral distribution curve of a blue SiC crystal is included for comparison (this curve depends on temperature). (See reference 1.)

3. EXPERIMENTAL RESULTS ON THE GREEN LIGHT EMISSION

(a) Spectral Distribution

The spectral distribution of the emitted light was measured by using a photomultiplier and various filters, as described previously.¹ Figures 1 and 2 show spectral distribution curves at room temperature and -124°C . The various curves in Fig. 1 refer to different currents passed through the crystal at room temperature. It is evident that spectral distribution of the emitted light does not change with the current passed through the crystal. In Fig. 2 spectral distribution curves which were taken (a) from different sides of the crystal, and (b) at room temperature and -124°C , are compared. Since the light emitting area was located close to the surface on which the catwhisker was placed, the light emission had to penetrate through a much thicker layer of the crystal in the case of the dashed-line curve than in the case of the solid-line curve. The fact that the spectral distribution is practically the same from either side of the crystal indicates that light absorption in the crystal is of little influence on the shape of the spectral distribution measured.⁵

Comparison of the spectral distribution curves at room temperature and at -124°C shows that spectral distribution of the green crystal does not depend on temperature in this range. In Fig. 2, the spectral distribution of light emission from a blue SiC crystal¹

⁵ R. W. Sillars [Phys. Rev. 85, 136 (1952)] has recently suggested that the spectral distribution of the emitted light is modified by the absorption of the crystal. Sillars observed the light emitted at point contacts. We have selected for our measurements crystals with light emitting areas (due to p - n -boundaries) which were much larger than the point contacts.

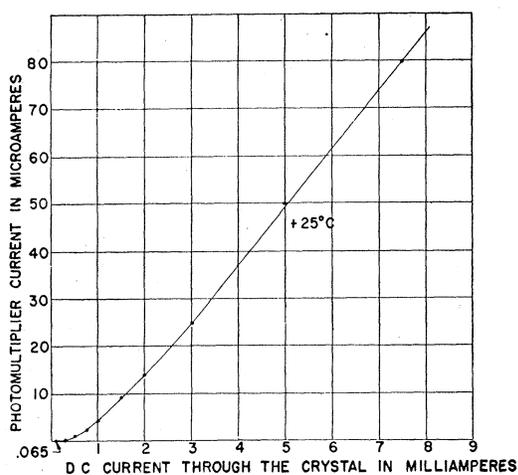


FIG. 3. Intensity of emission (expressed by the photomultiplier current) as a function of the current through the crystal at room temperature.

is included for comparison. The light emission in the blue crystal consisted of two bands, one with a maximum at 0.61 micron, the other with a maximum at 0.55 micron. When the temperature is lowered the emission band at 0.55 micron is enhanced more than that at 0.61 micron.

(b) Light Emission as a Function of the Current Passed

Since spectral distribution of the emitted light from the green crystal is independent of the current through the crystal and of the temperature (Figs. 1 and 2), the photomultiplier current is proportional to the intensity of the emitted light. Figure 3 shows the photomultiplier current as a function of the current passed through the crystal (catswhisker negative) at room temperature. For crystal currents larger than 1 ma, the light (as

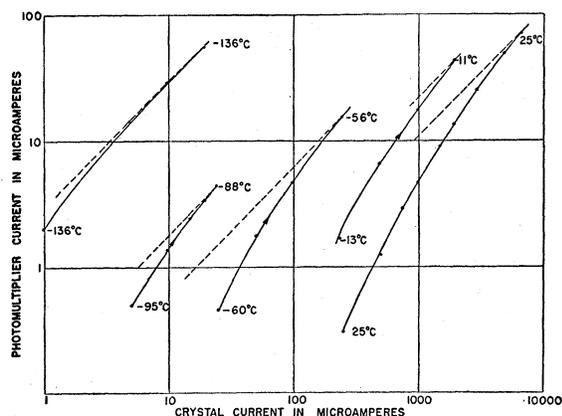


FIG. 4. Double logarithmic plot of the intensity of light emission (expressed by the photomultiplier current) as a function of the current passed through the crystal. Temperature of measurement is indicated in the figure. The dotted lines have a slope which corresponds to proportionality of the light intensity with the current passed through the crystal.

expressed by the photomultiplier current) can be approximated by the relation:⁶ $i_{\text{phot}} = bi_{\text{cryst}} - a$, where a is of the order of 700 microamp and $b = 1.2 \times 10^{-2}$. Thus for crystal currents larger than 1 ma the efficiency of light emission expressed by $i_{\text{phot}}/i_{\text{cryst}}$ approaches a constant value b ; whereas for crystal currents smaller than 1 ma the efficiency increases markedly with increasing current. This is seen more clearly from the double logarithmic plot of light intensity (expressed by photomultiplier current) vs crystal current (Fig. 4). The various curves refer to different temperatures. Since the curves were taken while warming up the crystal from -136°C to room temperature, the temperature of the crystal increased somewhat (as indicated in the figure) while taking the measurements for a

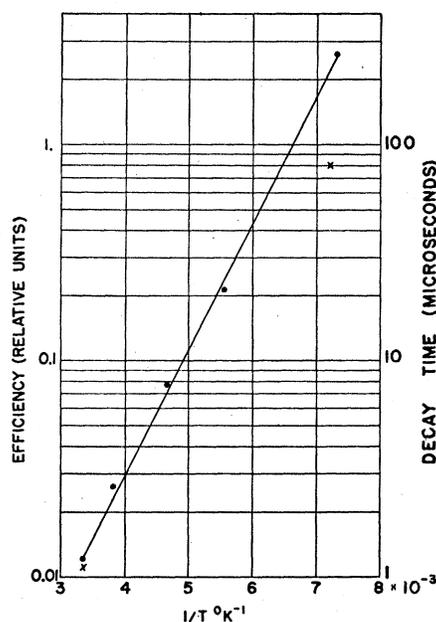


FIG. 5. Semilogarithmic plot of the values of efficiency corresponding to the dotted lines of Fig. 4 as a function of inverse absolute temperature. The straight line obtained indicates an exponential dependence with an activation energy of 0.118 ev. The two points marked by crosses are the time constants of the light emission.

particular curve. A slope of 45 degrees would indicate that the efficiency is independent of the current through the crystal. It seems that a slope of 45° is approached at higher current densities (the dotted lines have slopes of 45 degrees). At low current densities, the slopes become steeper. Relative values of efficiency have been calculated from the straight lines shown in Fig. 4. These values were plotted on a semilog scale against reciprocal absolute temperature (Fig. 5). A straight line is obtained which shows that the efficiency increases with decreasing absolute temperature by a Boltzmann factor $\exp(-T_0/T)$, with $T_0 = 1370^\circ\text{K}$ corresponding to an activation energy of $U = kT_0 = 0.118$ ev.

⁶ A similar behavior has been found in the case of light emission from blue SiC crystals.

(c) Absolute Value of the Efficiency of Light Emission

The absolute value of efficiency is defined as the ratio: light quantum emitted per electron passed through the crystal. Knowing the spectral distribution of the emitted light and the spectral sensitivity of the photomultiplier, the absolute value of the efficiency can be calculated. The efficiency at room temperature for the particular crystal under investigation was found to be 2×10^{-6} quanta/electron. This value is of the same order of magnitude as that reported previously for a blue SiC crystal. This coincidence is accidental; at other temperatures the efficiencies differ in value. The efficiency of the pale green crystal under discussion increases with decreasing temperature (see Fig. 5) and reaches at $T = -134^\circ\text{C}$ a value of about 2×10^{-4} quanta/electron. The temperature dependence of the efficiency of light emission intensity of the crystal under investigation can be written in the form $Ce^{1370/T}$, with $C = 2 \times 10^{-8}$ quanta per electron in the temperature range $140^\circ\text{K} < T < 300^\circ\text{K}$. Extrapolation to lower temperatures shows that an efficiency of about unity should be approached at $T \approx 80^\circ\text{K}$ (about liquid air temperature).

(d) Response Time

The response time of the light emission was investigated as follows: A square current pulse was passed through the crystal. The shape of the photomultiplier current caused by the light emitted from the crystal was inspected on an oscillograph. Figure 6 shows photographs of the pattern on the oscillograph corresponding to current pulses of different magnitude passed through the crystal. The temperature of the base plate on which the crystal was mounted was -140°C . The amplification of the photomultiplier current was adjusted to give traces of approximately the same height at the oscillograph. The shape of all traces is identical, independent of the magnitude of the current pulses used. The rise curves and the decay curves shown in the figure can be represented by functions $1 - e^{-t/\tau}$ and $e^{-t/\tau}$, respectively, with $\tau = 80$ microseconds. Measurements at room temperature also gave an exponential time dependence. Again the decay time was independent of the height of the current pulse. The decay time at room temperature was only 1.15 microseconds. The values of the decay time at room temperature and at -140°C are plotted in Fig. 5, together with values of efficiency of light emission. It will be noted that the decay time shows a temperature dependence quite similar to that found for efficiency.

4. SOME ADDITIONAL DATA ON THE LIGHT EMISSION FROM A BLUE SiC CRYSTAL

The observations described in what follows were made on a blue SiC crystal. The crystal was of the *p*-type except for a thin *n*-type region of about 4 mm² area on one face. A yellow light was emitted with the

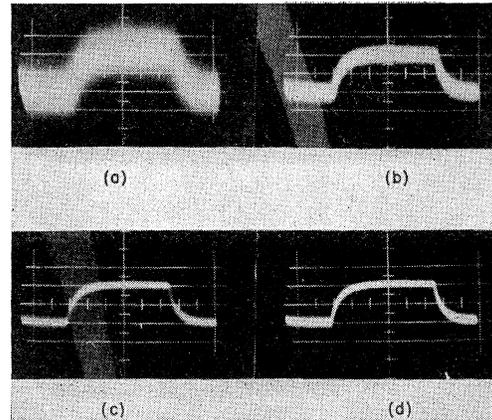


Fig. 6. Shape of the light pulse emitted from a green SiC crystal at -140°C when passing a square current pulse: 900 microseconds duration, and 500 cps repetition rate. Amplitude of current pulse: (A): 3, (B): 8, (C): 12, (D): 17 microamps; dc bias current: 10 microamps. The vertical amplification was adjusted to obtain patterns of about the same height.

passage of the current in the forward direction over the *p-n*-barrier. An effort was made to eliminate contact resistance in order to find the threshold voltage of the light emission for the intensity detectable by the eye. A nonrectifying base contact was made by plating zirconium on the base of the crystal by thermal dissociation of Zr hydride in a vacuum.⁷ Probe measurements showed that the base contact resistance was less than 0.2 ohm (area of the contact about 0.5 cm²). The other contact consisted of four steel catwhiskers connected in parallel and placed on the *n*-type layer. The current-voltage characteristic of this arrangement is shown in Fig. 7. The voltage at which light emission visible to the eye begins is marked by an arrow. Notice the change in slope in the characteristic at this voltage. Such a change has been observed earlier by others.⁸

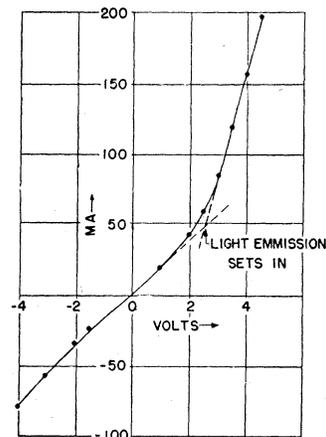


Fig. 7. Current voltage characteristic of a blue SiC crystal with *p-n*-barrier. The arrow marks the voltage between the electrodes of the crystal above which light emission is observed by the dark adapted eye.

⁷ C. S. Pearsall and T. K. Zingesser, unpublished Massachusetts Institute of Technology Technical Report No. 104 (1949).

⁸ O. Lossev, Physik. Z. 32, 695 (1931); B. Claus, Ann. Physik 11, 331 (1931); 14, 644 (1932).

A more exact determination of the threshold voltage for light emission at the barrier was made. A probe was placed on the light emitting surface and the area around the probe was inspected microscopically. The voltage between the current carrying contacts was increased until light emission became visible to the dark adapted eye in the area around the probe. The corresponding voltage at the contact was 1.8 volts. This voltage is less than that corresponding to the energy of the light quanta emitted (2 eV). The difficulties encountered in probing a *p-n* boundary grown under uncontrolled conditions do not permit one to put too much emphasis on this small difference. Any excess of energy emitted over energy supplied by the battery must have been taken up by lattice vibrations. This should lead to a cooling effect, as in the case of the well-known Peltier effect.

5. DISCUSSION

In the study of light emission one is concerned with (a) the excitation process (in our case, carrier injection) and (b) the emission process.

The carrier injection should not differ fundamentally from that known through studies of the transistor effect.⁹ The emission process should not differ fundamentally from that occurring in ordinary phosphors.¹⁰

In what follows we shall discuss briefly some of our experimental results from the point of view of carrier injection and phosphorescence. Unfortunately, we are unable at present to produce artificial SiC crystals of known composition. Details of the barrier structure and of the activator centers in the crystals investigated are not known so that any interpretation is only tentative.

(a) Remarks on the Injection Process

The shape of the current-voltage characteristic (Fig. 7) suggests that the current over the barrier consists of two parts. One part is proportional to the voltage at the contact and passes the barrier layer essentially unrectified contributing nothing to the light emission. In the blocking direction at low voltages, this part constitutes the entire current. The other part which does lead to light emission sets in measurably above a threshold voltage in the forward direction and is absent in the blocking direction. We are inclined to ascribe the former to conduction on impurity levels¹¹ (or to some other process involving strongly disordered structure), and the latter, to carriers injected across the barrier. The presence of a current which does not lead to excitation and which at low current densities is

⁹ W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand and Company, Inc., New York, 1950).

¹⁰ H. W. Leverenz, *Luminescence of Solids* (John Wiley and Sons, Inc., New York, 1950).

¹¹ Presence of such a current was suggested by G. Busch (Helv. Phys. Acta **10**, 167 (1946)) in order to explain measurements of the temperature dependence of thermoforce and of Hall effect in SiC crystals.

a large fraction of the total current, may be one reason for the observed dependence of the efficiency on current density at low currents (Fig. 4).

(b) Remarks on the Emission Process

A dependence of efficiency on current density may be inherent also in the emission process. It is known from experiments on the luminescence of ZnS- and other phosphors that the efficiency of the emission process may increase with increasing intensity of excitation.¹² The dependence of the efficiency of excitation becomes more pronounced at lower intensities of excitation and at higher temperature and may be caused by the presence of so-called "killers."¹³ "Killers" are centers which enable radiationless transitions of excited electrons. A well-known killer in ZnS-phosphors is Fe. Traces of Fe were present in the pale green crystal under investigation.

It is customary to consider the following processes when discussing the time dependence of emission of phosphors:

(1) The lifetime of the free electron before being captured; the capture may take place at traps (1a), at activator centers in an excited state (1b), or at killer centers (1c).

(2) The electron may be re-emitted into the conduction band from the traps (2a), or from the excited states of the activation centers (2b).

(3) The electrons captured in an excited state of the activator may transfer to the ground state under light emission (3a) or under dissipation of its energy in heat (3b). The electron captured at a "killer center", loses its energy into heat (definition of "killer").

Any one of these steps (1), (2), (3) may determine the decay time. Some of the steps (1b), (1c), (2b), (3a), (3b) account for the efficiency. In our case both efficiency and decay time are strongly temperature dependent. Only the processes (2a), (2b), and (3b) depend in general strongly on temperature. This suggests that at least one of the processes (2a), (2b), and (3b) are involved in the efficiency and decay time. We have observed that efficiency and decay time have about the same temperature dependence. This suggests that the same step is of importance for efficiency and decay. Trapping influences only decay but not efficiency tentatively and seems therefore of no importance. We conclude that either (3b) or (2b) (or both) account for the observations on efficiency and decay.

Let the relative probability of a free electron to be captured by an activator (instead of being captured by a killer) be f . Let the probability for a radiative transition per unit time of an electron from the excited state of the activator to the ground state (step 3a) be p , that of re-emission to the conduction band (step 2b) p' , and that of nonradiative transitions to the ground

¹² N. Riehl, Z. Tech. Physik **20**, 152 (1939); J. H. Gisolf and F. A. Kröger, Physica **6**, 1101 (1939); Urbach, Urbach, and Schwartz, J. Opt. Soc. Am. **37**, 122 (1947); S. Robert and F. Williams, J. Opt. Soc. Am. **40**, 516 (1950).

¹³ Urbach, Urbach, and Schwartz, J. Opt. Soc. Am. **37**, 122 (1947).

state (step 3b) p'' . Both p' and p'' are of the type $s \exp(-E/kT)$ with different numerical values for s and E . In general, only one of the processes (2b) or (3b) will be of importance owing to differences in the numerical values of E . The efficiency is then¹⁴ $\epsilon = fp / [p + s \exp(-E/kT)]$, and the decay time τ of phosphorescence: $1/\tau = p + s \exp(-E/kT)$. Our measurements covered a temperature range in which ϵ and $1/\tau$ were strongly temperature dependent. This implies that $p \ll s \exp(-E/kT)$. Thus $\epsilon \approx fp / [s \exp(-E/kT)]$, $1/\tau \approx s \exp(-E/kT)$, and $\epsilon/\tau = fp$.¹⁵ Using the measured values $1/\tau \approx 10^6 \text{ sec}^{-1}$ at room temperature, $\epsilon = 2 \times 10^{-6}$ quanta/electron at room temperature, and $E = 0.114 \text{ ev}$, we obtain $fp \approx 2 \text{ sec}^{-1}$ and $s \approx 10^8 \text{ sec}^{-1}$. The value of s is of the same order of magnitude as that frequently obtained in other phosphors from glow and decay

¹⁴ Consideration of recapture of an electron of an activator after the release from an excited state introduces only a small modification of the equation, if $f \ll 1$.

¹⁵ The close relationship between the temperature dependence of efficiency and that of decay time has been observed on Mn-activated zinc silicate phosphors by F. A. Kröger and W. Hoogenstraaten [*Physica* **14**, 425 (1948)].

experiments.¹⁶ Separation of f and p would be possible if efficiency and decay measurements were extended to sufficiently low temperatures where the factor $\exp(-E/kT)$ becomes negligibly small. Then efficiency and decay time should be independent of temperature: $\epsilon \approx f$ and $1/\tau \approx p$. Unfortunately with our present equipment we were not able to reach this temperature range.

The temperature U calculated from Fig. 5 is of the same order of magnitude as the ionization energy of conduction observed by G. Busch¹⁷ for some pale green crystals (e.g., crystal 12a, $E_2 = 0.120 \text{ ev}$ in his Table I). It would be very interesting to investigate a possible relation between activation energy of conduction and that of efficiency of phosphorescence on the same crystal. Crystals with homogeneous impurity distribution would be necessary, however.

We are indebted to Mr. J. Mellichamp for performance of the spectroscopic analysis.

¹⁶ See, e.g., J. Randall and M. Wilkins, *Proc. Roy. Soc. (London)* **A184**, 366 (1945).

¹⁷ G. Busch, *Helv. Phys. Acta* **10**, 167 (1946).

Diurnal Variations in the Intensity of Cosmic Rays Underground*

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The number of coincidences between two trays of Geiger-counters located at a depth of $8.46 \times 10^4 \text{ g cm}^{-2}$ underground was recorded each hour, and these data were analyzed for variation of cosmic-ray intensity with solar and sidereal time. (A total of $7.4 \times 10^5 \mu$ -mesons was observed whose average energy is estimated to be $2 \times 10^{11} \text{ ev}$.) In each case the standard deviation of the observed coincidence rates from the mean rate is not larger than the standard deviation expected from a normal distribution. The first harmonic amplitudes of the solar and sidereal variations indicate that the data are equally consistent with an assumed daily sinusoidal variation in the coincidence rates of ~ 0.5 percent and with the absence of such variation. The difficulties involved in deducing directional properties of the primary cosmic radiation from harmonic analysis of variations in secondary radiation underground are discussed.

THE investigations of Elliot and Dolbear¹ indicate the existence of small solar and sidereal diurnal variations in the intensity of the hard component at sea level. They interpret these results as due to the non-isotropic incidence of primary cosmic rays. In the course of an investigation of the correlation between variations in atmospheric temperatures and variations in the intensity of high energy μ -mesons observed underground (to be reported at a later date), we have collected hourly counting rates for these particles which might be expected to reflect variations in the intensity of primaries of high energy.

* This work has been partially supported at different stages by the Air Force Cambridge Research Center and the joint program of the ONR and AEC.

¹ H. Elliot and D. W. N. Dolbear, *J. Atmos. Terr. Phys.* **1**, 205 (1951); H. Elliot, *Progress in Cosmic-Ray Physics*, edited by J. G. Wilson (North-Holland Publishing Company, Amsterdam, 1952), Chap. VIII.

The coincidences between two trays of Geiger counters (each tray 24 in. \times 90 in.) located at a depth of $8.46 \times 10^4 \text{ g cm}^{-2}$ in a salt mine in Detroit, Michigan, were recorded each hour and analyzed for diurnal variations. An inch of Pb was placed between the trays to effectively eliminate coincidences due to local radioactivity and the accidental counting rate ($\sim 1.3 \text{ hr}^{-1}$) was measured periodically (showing negligible time variations) for use in correcting observed counting rates. During the year ending March 31, 1952, 7.4×10^5 counts were recorded with a mean corrected counting rate of 107.8 hr^{-1} . The average energy of μ -mesons observed at the depth of the mine has been estimated to be $\sim 2 \times 10^{11} \text{ ev}$.²

The variation of intensity with solar time is shown in Fig. 1 and with sidereal time in Fig. 2. The errors are

² C. A. Randall, thesis, University of Michigan (1950) (unpublished).

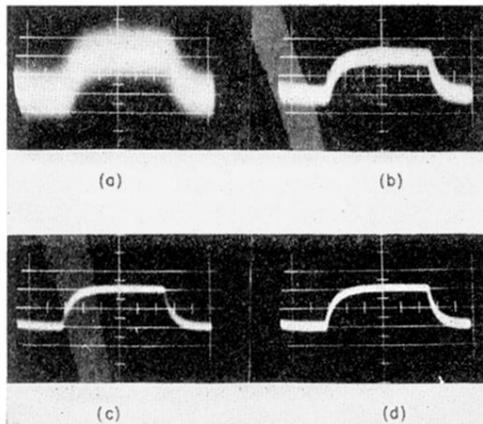


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