THE LUMINESCENCE OF KUNZITE.

BY E. L. NICHOLS AND H. L. HOWES.

THAT the variety of spodumene known as kunzite is phosphorescent has been known almost from the day of its discovery. In August, 1903, Geo. F. Kunz[1] described its occurrence and properties and in September of that year Baskerville[2] who was making an exploration of the optical properties of the minerals in the American Museum of Natural History proposed the name of kunzite for this substance and in the course of his description stated that although it showed no sign of fluorescence or phosphorescence when exposed to ultra-violet light, X-rays excited it to a prolonged whitish phosphorescence.

Kunz and Baskerville[3] subsequently tested the luminescence of numerous minerals and reported that kunzite was wonderfully phosphorescent under the action of radium; that ultra-violet light, contrary to Baskerville's first observation, excited certain specimens to prolonged luminescence and that X-rays affected all the crystals of that mineral which were examined.

A writer in Nature, presumably Mr. F. Soddy,[4] speaks of the excitation of kunzite by radium as due chiefly to the β rays and mentions also the powerful excitation obtained by kathodo-bombardment.

Pochettino[5] in his extended investigation of the luminescence of minerals included the spodumenes and in particular certain samples of kunzite. He found this substance feebly fluorescent under the action of light with the emitted rays polarized.

Under the kathode rays he was able to observe a spectrum consisting of a very strong broad band extending from λ .690 to λ .515 and a weak one from .48 to .42. The band of longer wave-length was of protracted phosphorescence while that in the blue disappeared "instantly" upon cessation of the excitation. Pochettino noted further the phenomenon of thermo-luminescence at 235° C.; in which case the rays were not polarized. The power of emission ceased at about 400° C.

[1] Kunz, Science, 18, p. 280 (1903).

[2] Baskerville, Science, 18, p. 303 (1903).

[3] Kunz and Baskerville, Science, 18, p. 769 (1903).

[4] "F. S.," in Nature, 69. p. 523 (1904).

[5] Pochettino, Il Nuovo Cimento (V), 18, p. 245 (1909), and (VI), 1, p. 21, 1911.

It was the purpose of our experiments to study more in detail the location and character of these bands, to seek for the absorption bands which are generally if not universally associated with fluorescence and to determine the law of decay.

FLUORESCENCE.

The crystals at our disposal appeared to be of two varieties: (1) Those with the pink or rose-lilac hue generally considered to be characteristic of kunzite and (2) crystals nearly colorless but with a suspicion of a green- or aqua-marine tint.

Under the action of kathode rays both were strongly fluorescent but the colors differed. The pink crystals glowed with the powerful yellow-red light described by previous observers, which resembles nothing more

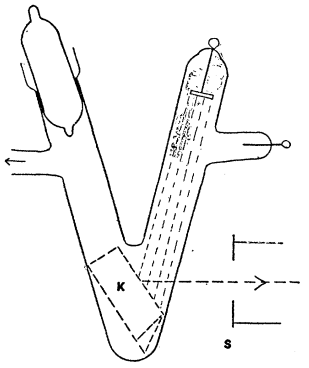

Fig. 1.

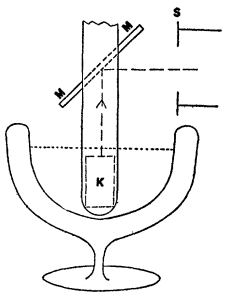

Fig. 2.

closely than the light from some transparent body, as quartz or glass at a temperature of about 900° C. The colorless specimens were of a rose-violet hue.

Observed with a hand spectroscope this difference is seen to be clearly due to the relative strength of the fluorescence bands. In the case of the colorless crystals the blue band is much stronger and its intensity is such as to notably modify the color of the fluorescent light.

The specimen (*K*) to be studied was placed in a V-shaped vacuum tube as shown in Fig. 1 and the face, bombarded from above by kathode rays, was observed with a spectrophotometer, the slit of which is shown at *S*.

The strong broad band lying between .7 μ and .5 μ was readily measured spectrophotometrically and was found to have the well known and typical form observed in numerous other fluorescent substances and depicted in previous papers.[1]

[1] Nichols and Merritt, PHYS. REV. (1), Vols. XVIII., XIX. and XXI.

The curve of distribution of intensities (*B*, Fig. 3) is as usual nearly symmetrical but somewhat steeper towards the violet. The well-defined crest is at .590 μ. There is nothing to suggest that it is a composite of overlapping bands.

To determine the effect of cooling which is known in many cases to modify the character of the fluorescence spectrum, the tube was immersed in liquid air to a level above that of the crystal as shown in Fig. 2. In this case observations were made by placing a mirror *M* between the arms of the vacuum tube so as to reflect the fluorescent light, emanating vertically from the crystal, into the collimator slit at *S*.

The appearance of the specimen when thus cooled is distinctly redder to the eye and this impression is verified by the spectrophotometric measurements. The curve (*A*, Fig. 3) which is somewhat narrower, has

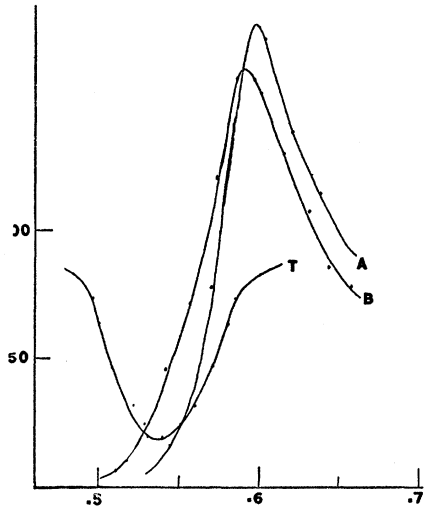

Fig. 3.

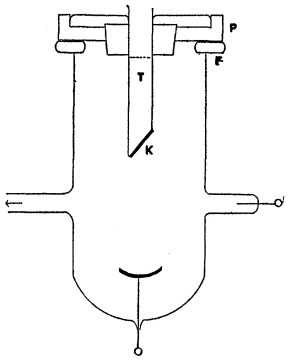

Fig. 4.

its crest shifted towards the red to .598 μ and indicates accession of the longer wave-lengths together with marked diminution on the violet side. There is no indication of even a partial resolution into a group of narrow bands.

That a crystal, thus situated in vacuo within a glass tube and subjected to the heating effect of even a very moderate kathodic bombardment, will be in thermal equilibrium at some temperature considerably above that of the liquid air surrounding the tube is obvious. That this difference of temperature may be more than 100° C. is indicated by previous experience with substances subjected to somewhat similar conditions.

In a case which was described in a paper presented before the American Physical Society, the character of the spectrum afforded a sufficient criterion on which to base this estimate.

A modification of the apparatus enabled us to determine the fact that even at a temperature really approaching that of liquid air no further marked modification in the position or appearance of the band occurred. For this purpose a small piece of the kunzite was powdered and cemented to the outer surface of a test-tube the bottom of which had been softened by heat and obliquely flattened so as to form a convenient target for kathode rays. This test tube was mounted within a vacuum tube of the form shown in Fig. 4 in which P is a cast-iron plate ground to the flange F of an open-mouthed glass tube having a kathode at the bottom. The test tube T was inserted through a rubber stopper fitted to a central opening in the iron plate. When a proper vacuum had been attained liquid air was poured into the test tube cooling the coating of powdered kunzite at K. The fluorescence of K could be observed in the manner previously described and any change in the character of the spectrum noted. The measurements while less satisfactory than those indicated in Fig. 3 were in essential agreement with them.

The fluorescence band of shorter wave-length which begins at .49 μ and extends into the violet, is less favorably situated for study with the spectrophotometer and we contented ourselves with an estimation of its extent and general character by a photographic method. Spectrograms were taken, using both the pink and white crystals, upon two different plates so as to lessen errors due to the selective sensitiveness of the photographic film. The negatives indicated that the same bands were present in both cases but, as had already been noted by visual observations, were of very different relative brightness. The blue band was found to lie between .49 μ and .40 μ with a crest at approximately .432 μ. Since the location of the crest by visual inspection was rather uncertain one of the negatives was measured as to density, step by step at intervals of 1 mm. by means of a photoelectric cell. This determination which was kindly made for us by Mr. W. G. Mallory gave boundaries and location of the crest in excellent agreement with our visual estimates. The form of the curve indicated, as in the case of the red band, that if complex this band must also consist of close and completely overlapping components. This band is shown graphically in Curve B of Fig. 5, in which however the relative intensities of the two bands are only approximately indicated.

To determine the strength of the two bands observations were made with the spectrophotometer; the brightness of the crests of the red and blue bands of the white and the pink kunzite under kathodo-excitation

being compared respectively with the corresponding regions in the spectrum of the acetylene flame. It was found that when the crest of the band at .690 μ in the case of the pink kunzite was made equal in brightness to the same region in the acetylene spectrum, the intensity of the crest of the blue band at .432 μ was about 43 per cent. of that of the corresponding region in the acetylene spectrum whereas the white crystal under like conditions had a blue band about 2 per cent. brighter than the acetylene spectrum. In other words when the red bands of the two varieties are equally bright the blue band of the white kunzite is about 2.33 times as intense as that of the pink variety.

ABSORPTION.

By analogy with numerous substances previously studied one would expect to find absorption bands in kunzite associated with the two fluorescence bands, of approximately the same width and displaced towards the violet. Looking through a thickness of several millimeters of the substance, however, with a hand spectroscope of small dispersion nothing of the kind is perceptible. The crystal appears to be of about the transparency of ordinary white glass and as free from selective absorption. Looking lengthwise through a crystal of considerable size which afforded an absorbing layer of about 5 cm. the color of the transmitted light is distinctly purple and the spectroscope reveals a rather vague band which is by no means opaque even in the center. Spectrographs bring it out clearly but are not suitable for measurement because of the selective absorption of the film, which in all the plates at our disposal has a region of more or less pronounced weakness which overlaps this band on the side towards the violet. By spectrophotometric meas-

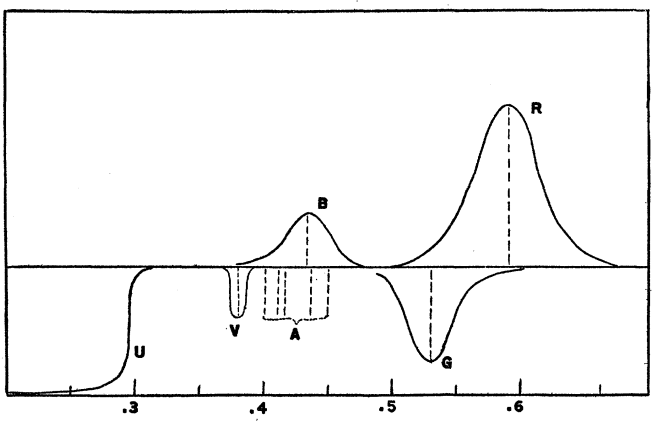

Fig. 5.

urements this band was easily mapped. It extends from .64 μ to .49 μ with a well-defined crest at .538 μ and, as may be seen from Curve *T*, Fig. 3, which depicts approximately the transmission of the crystal, it overlaps the violet edge of the fluorescence band *B*.

Photographs show a series of narrow absorption bands (*A*, Fig. 5) at .4019, .4117, .4170, .4375 and .4501 μ. These have a width of only about 70 Ångström units. Beyond .4 μ this thick crystal layer became rapidly opaque making the photographic exploration difficult. By placing the crystal transversely across half of the slit of a quartz spectrograph; the transmitting layer being about 4 mm., it was possible to obtain photographs extending to .3 μ, at which point even this thin layer became abruptly opaque as is indicated by Curve *U* in Fig. 5. Such photographs however failed to show the absorption bands already detected and located.

To determine if possible whether a broad band associated with the blue fluorescence existed, a series of spectrograms through crystals of such intermediate thickness as were available were made. One of these photographs, taken through a layer of 15 mm. revealed such a band lying between .3750 and .3875 μ with a crest at .380 μ. This band which lies in the usual relation to the blue band is shown at *V* (Fig. 5).

Fig. 5, to which reference has been made, is intended to depict in a rough way the fluorescence and absorption of kunzite in so far as is possible from the present study. In the diagram the fluorescence bands (*R* and *B*) are shown above the base-line and the absorption bands *A* and *V* below. Whether a group of narrow fluorescence bands associated with the group *A* exists we have not thus far been able to determine. If so they would probably be comprised within the band *B*, and unless very brilliant, would be indistinguishable.

PHOSPHORESCENCE.

The phosphorescence of kunzite has certain interesting characteristics. While it is of comparatively long duration being easily discernible for several minutes after adequate excitation, decay is at first of extraordinary rapidity so that measurable brightness remains only in cases where the initial intensity of excitation is very great.

To determine the law of decay a simple photometer was improvised. It consisted of a small Lummer-Brodhun cube *L*, Fig. 6, mounted at the junction of two short tubes *C* and *D*. Light from the phosphorescent body *K* passed through a yellow screen *S* and through the central transmitting field of the cube to the eye which was focused upon the interface by means of an eyepiece of low power at *E*. The reflecting field was

illuminated by an acetylene flame with diaphragm (F) which was mounted upon a photometer bar (BB) two meters in length. The brightness of this comparison field was reduced by the interposition of a dense milk-glass screen at M and a sufficient color match was secured by means of an amber screen at Y.

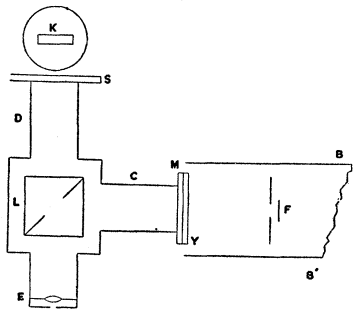

Fig. 6.

This arrangement had a range of about 180 to 1 and by substituting for the dense milk glass a ground glass at M, this could be increased to 18,000 to 1.

With the milk glass screen that part of the curve of decay from about 0.4 second after close of excitation to 60 seconds could be determined. The times of beginning and close of excitation were recorded on a chronograph and by shifting the comparison flame to successive predetermined positions on the bar and recording the times when a photometric balance was passed for each position ten or twelve points on the curve were obtained after a single excitation of the crystal.

The tube containing the kunzite crystal was connected to a Gaede mercury pump in continuous operation and under these conditions a reasonable constancy of intensity of excitation was secured.

Curve D in Fig. 7 is a typical example of the numerous curves obtained with this apparatus. It shows only a small portion of the period of rapid decay immediately following the end of excitation. To include the record of the first half second of time it would be necessary to extend the ordinate of intensities about three hundred times the height of the existing diagram. Using the reciprocal of the square root of intensity as ordinates the data give the linear branches 2 and 3 in the same figure.

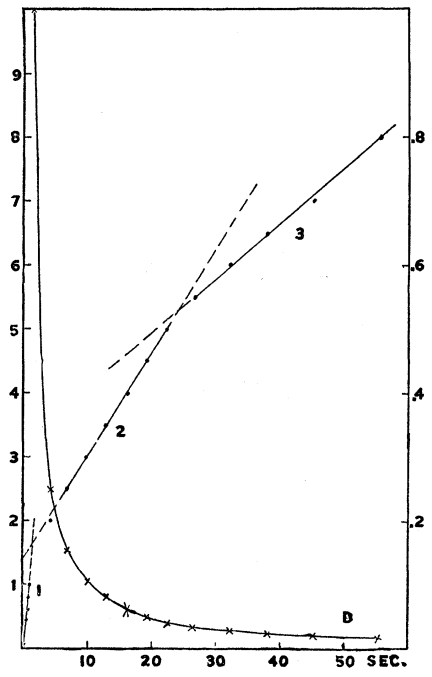

Fig. 7.

As is well known it has been customary to describe the decay curves of Sidot blende, willemite and numerous other substances, thus plotted, as composed of two such linear processes.[1] Lenard[2] and others have contested the linear character of the initial process although the determinations of Waggoner[3] and of Zeller[4] whose measurements covered the first few hundredths of a second, an interval impossible to observe by the usual methods, showed a linear relation between $I^{-1/2}$ and time.

In the case of kunzite the line marked "2" in the diagram clearly does not represent the initial process of the decay of phosphorescence for its intercept corresponds to an intensity far below the brightness of the substance at the close of excitation. Observations made six tenths of a second after the beginning of decay consistently gave measured intensities much greater than this intercept would indicate.

Since the excitation was by kathodo-bombardment it was easy to measure the initial brightness directly by substituting the ground glass screen and thus increasing the brightness of the comparison light one hundred times. It was also possible with this screen to determine the brightness for times ranging between 3/10 sec. and 6/10 sec.

These values plotted for $I^{-1/2}$ and time lie in a straight line which passes through the intercept for the initial brightness as measured and constitute the process marked (1) in Fig. 7. Since this process gives the true value of the intensity at the close of excitation it may be termed the initial process. It is shown on a larger scale in Fig. 8.

This result is quite in accordance with the experiments of Waggoner and of Zeller whose initial process was also linear and of a steeper slope than what had been taken for the first process in previous studies of decay of long duration.

Kunzite differs from many phosphorescent substances in its comparative inactivity to photo-excitation. A spark discharge between iron or zinc terminals sufficient to leave willemite, Sidot blende, and numerous other substances brilliantly phosphorescent has so feeble an effect on kunzite that special precautions are necessary to enable any after effect whatever to be discerned. Baskerville and Kunz[5] noticed photo-phosphorescence in the case of the white variety only and not at all in pink crystals. The latter, however, are capable of excitation as may be determined by passing a bundle of rays from the carbon arc or mercury lamp through a light

[1] Nichols and Merritt, PHYS. REV., XXV., p. 362; C. A. Pierce, PHYS. REV., XXVI., pp. 312 and 454.

[2] Lenard, Annalen der Physik, XXI., p. 641 (1910).

[3] C. W. Waggoner, PHYS. REV. (1), XXVII., p. 209.

[4] Carl Zeller, PHYS. REV. (1), XXXI., p. 367.

[5] Baskerville and Kunz, l. c.

filter transparent only to blue and the shorter waves, and then through the crystal to be examined. The ruddy path of the beam is clearly discernible particularly when viewed through an amber or yellow glass. The exciting effect of the individual lines of a mercury arc spectrum from .4359 μ to .3663 μ can also be detected with proper precautions for the exclusion of stray light.

The appearance of dichroism in the pink variety is probably due, in part at least, to its fluorescence. The disappearance of color when the crystal is viewed through a Nicol prism occurs at an angle for which the fluorescent light which as Pochettino[1] has shown is polarized, would be cut off. The pink color disappears, moreover, when the crystal is illuminated by rays deficient in exciting power.

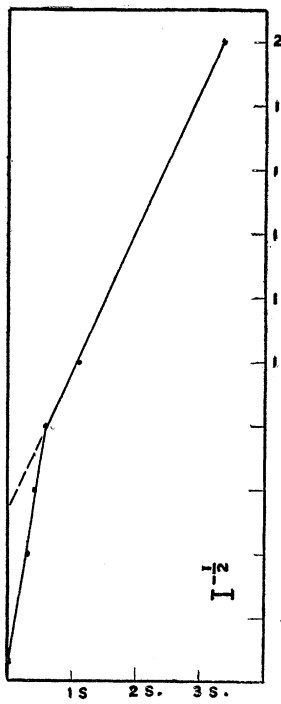

Fig. 8.

May it not be that the feeble photo-excitation of kunzite, certain calcites, etc., is due to their transparency even in the absorption band? Kunzite is almost impervious to X-rays and responds to their excitation while the kathode rays, which are completely absorbed, produce the most powerful effect.

Like most, if not all, substances whose phosphorescence is of long duration, kunzite requires an appreciable time to reach its maximum of excitation. Under kathodo-bombardment saturation is reached after a few seconds. The length of time required for the phosphorescence to decrease to 1/18,000 of the initial brightness was no greater after an excitation of five minutes than after ten seconds. Excitation of less than one second however produced phosphorescence of comparatively short duration, the time of decay to 1/18,000 being about one half that for the longer exposures. Under the feebler excitation by X-rays or when the sparks from a Holtz machine are caused to pass across the surface of the crystal it is possible to follow with the eye the gradual growth of the fluorescence.

We did not attempt to make a quantitative study of these phenomena because kunzite suffers fatigue under continued bombardment from which its complete recovery is slow. Indeed there is undoubtedly a permanent

[1] Pochettino, l. c.

effect which shows itself, as in many other substances, in a dullness and discoloration of the surface. Red and infra-red rays have no appreciable effect upon the degree of excitation or the rate of decay. In this respect kunzite differs from Sidot blende.

In all the measurements on phosphorescence the substance was viewed through a yellow screen (*S*, Fig. 6) in order to prevent blending of the light from the two bands. This was however an unnecessary precaution since the blue band is of exceedingly rapid decay as could easily be determined by observation through a blue screen. No after effect lasting as much as a tenth of a second could be detected.

In this respect kunzite is similar to the phosphorescent sulphides of Lenard and Klatt and it resembles them also in becoming inactive, according to Pochettino, at about 400°.

Throughout these experiments the important feature of polarization was ignored. That a detailed study of this aspect of the luminescence of kunzite would yield interesting results there is little doubt. Indeed the general subject of the polarization phenomena in luminescence, concerning which we have as yet only the suggestive data of Pochettino, J. Becquerel and a few other observers deserves further consideration.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
April 18, 1914.