Luminescence from Sodium Chloride*

William E. Spicer†

Department of Physics, University of Missouri, Columbia, Missouri

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The x-ray-induced luminescence from NaCl has been studied in the range from 2.1 to 5.2 ev and in certain cases correlated with optically induced luminescence. The intensity and spectral distribution of the x-ray-induced luminescence was found to be dependent on the previous heat treatment received by the crystal. Before heating, bands are present at 2.25, 3.1, and 5.0 ev; afterwards, strong new bands appear at 2.45 and 3.5 ev and the intensity of the 5.0-ev band is increased. Prolonged x-irradiation reduces most of the effects of heat treatment; however, following such prolonged x-irradiation, a relatively strong band is present at 2.9 ev.

In the heated crystals, it was found possible to induce the 2.45- and 3.5-ev bands by irradiating x-ray-colored crystals with light absorbed in the F band; thus indicating that these bands are probably due to electronic transition from the conduction band into lower lying levels. An afterglow due to the thermal ejection of the electrons from traps was found and studied in conjunction with the optically induced luminescence. The same bands were present in the optically induced luminescence as in the afterglow.

INTRODUCTION

IN view of the information which has been acquired concerning the absorption centers produced in NaCl by x-irradiation,[1] it seemed fruitful to study the luminescence which might be produced by the same means. In doing this, an attempt has been made to obtain an over-all picture of the luminescence phenomena rather than to make a more exhaustive study of any one phase of the problem.

Luminescence spectra produced in NaCl by x-irradiation,[2–4] cathode ray bombardment,[5] and optical excitation[6–8] have been reported. Although only rarely has the same band been reported by different workers, over half of the bands reported lie in the region from 1.9 to 2.45 ev; and three workers have reported a band at about 5.0 ev. Luminescence afterglow following x-irradiation has been studied and both exponential[9,10] and power law[4] decays reported. The luminescence emitted by electrons falling into halogen ion vacancies to form F-centers has been studied by Botden, Van Doorn, and Haven[11] and found to lie at about 1.05 ev.

EXPERIMENTAL TECHNIQUES

The dimensions of the crystals studied were about $10 \times 7 \times 3$ mm. These crystals were cleaved from large specimens obtained from the Harshaw Chemical Company. As luminescence might result from the presence of small quantities of heavy metal impurities, the samples were analyzed for these elements. Within the accuracy of the analysis, a few parts per hundred thousand, no such impurities were found. Two groups of crystals obtained two years apart, were studied. Essentially the same results were obtained from both.

A Perkin-Elmer Model 83 Universal monochromator, equipped with a fused quartz prism and a motor wavelength drive was used to disperse the luminescence. Upon leaving the monochromator, the luminescence was reflected by an aluminized front surface mirror onto a quartz light-guide which directed the radiation onto an RCA 1P28 photomultiplier held in a liquid air cryostat. Pulses created by individual photons were fed through an Atomic Instrument Company Model 205 linear preamplifier into a Berkeley Model 2810 counting rate meter. The output of the counting rate meter was recorded on an Esterline Angus Model AW recorder. All spectra have been corrected for the dispersion of the monochromator, reflectivity of the mirror, absorption of the quartz light-guide, and sensitivity of the photomultiplier.

Luminescence was induced by two methods: direct x-irradiation and optical irradiation of x-ray colored crystals. In the former case the crystal was placed in front of the x-ray tube, a Machlett AEG-50-T tube equipped with a tungsten target, a 1 mm beryllium window and operated at 40 pkv with 10-ma plate current. In the latter case, the crystal was first subjected to fifteen minutes of x-irradiation and then placed before the entrance slit of the monochromator. Optical filters were mounted in front and back of the crystal. By appropriate choice of these optical filters and the light sources, the crystal could be irradiated with light of a certain wavelength while luminescence induced in another wavelength could be observed. Great care was taken that the primary radiation was eliminated from the observed luminescence. Either an arc emitting a line spectrum or the radiation from a tungsten lamp dispersed by a Gaertner monochromator provided the exciting radiation.

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EXPERIMENTAL RESULTS

I. Spectra Taken under Continuous X-Ray Irradiation

Both the intensity and spectral distribution of x-ray-induced luminescence from the NaCl crystals were found to be dependent on the heat treatment and x-ray dosage which the crystal had received. Figure 1 shows the spectra obtained under x-irradiation from a crystal before and after it was heated for fifteen minutes at about 600°C (all data reported here were taken at room temperature). Before heating, bands were present at 2.25 ev, 3.1 ev, and 5.0 ev. The shapes of the two lower energy bands, particularly the 3.1-ev band, indicate that unresolved bands might lie on their high-energy sides. Following heating, strong new bands appeared at about 2.45 ev and 3.5 ev and the intensity of the band at 5.0 ev was greatly increased. The shape of the 2.45-ev band suggests that the 2.25-ev band was still present but unresolved. A relatively weak band seems to be present at about 2.9 ev.

The results shown in Fig. 1 were obtained for a crystal heated for fifteen minutes; however, the results differed very little for heating times varying between one minute and one hour. Also the spectra were essentially independent of the rate of cooling. For example two crystals heated to 520°C for 10 minutes, one of which was quenched in CCl₄ and the other cooled at a rate of 0.5°C/minute, had essentially identical spectra. The only difference was a reduction of about one-third in the intensity of the 3.5-ev band for the annealed crystal. Except for changes brought about by x-irradiation (discussed below), the effect of heating was found to be stable over the period of study (1½ years).
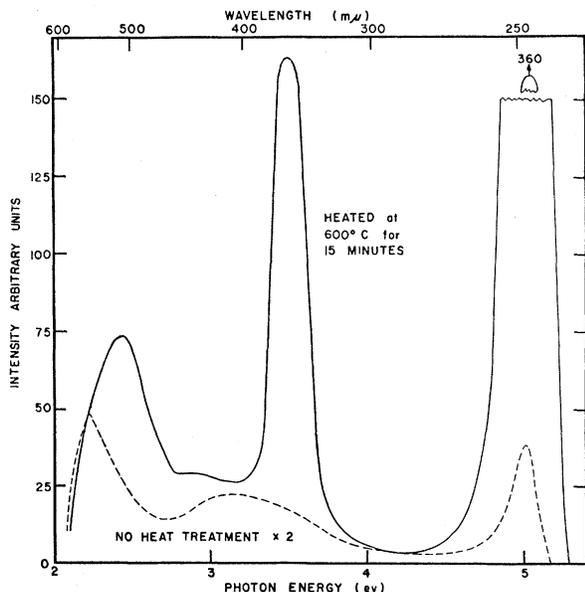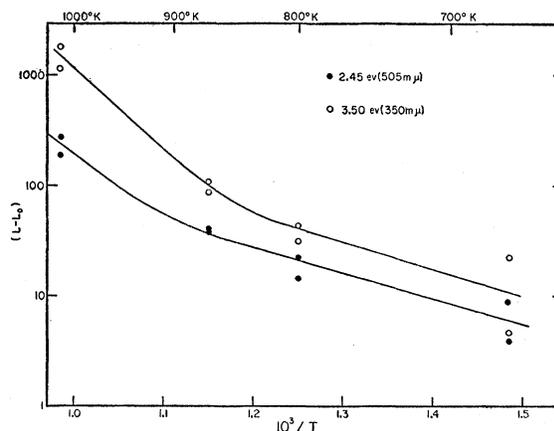
FIG. 2. Change in intense $(L-L_0)$ at 2.45 and 3.5 ev as a function of heating temperature.

To study the change of luminescence intensity as a function of the temperature of heating, crystals were heated for fifteen minutes at a given temperature and then removed to room temperature and allowed to cool. The peak intensities at 3.51 ev and 2.45 ev were measured before and after this treatment. Two crystals were heated at each temperature, thus giving two experimental points for each temperature. Figure 2 is a plot of the logarithm of the change in intensity, $(L-L_0)$, versus the reciprocal of absolute temperature. Despite the scattering of points the continuous growth in the strength of these bands with temperature is striking.

The effect of heating was not distributed uniformly throughout the crystal but decreased with distance from the surface. Since the x-ray penetration was only about 0.7 mm, it was possible to study this effect by cleaving away portions of the crystal. Figure 3 shows typical results obtained from a 4 mm thick crystal which was heated to 650°C. After spectrum 1 was obtained from the original face, first 0.85 mm and then 1.2 mm were cleaved from the crystal and curves 2 and 3 were taken. Although there is a gradual, over-all, decrease in intensity with depth, the striking effect is the decrease in the 3.51-ev and 2.45-ev bands relative to the rest of the spectrum. Notice that, after cleaving, the 2.25- and 2.45-ev bands seem to be of comparable intensity.

The depth effect has also been studied as a function of the time of heating. To do this, crystals (2.85 mm thick) were heated for various lengths of time at approximately 600°C, quenched in CCl₄, and then cleaved in two. Thus, spectra could be taken from the newly cleaved face and from the original face. The differences between the crystals heated for 2 and 50 minutes were striking. For a crystal heated for two minutes, the intensities of the 2.45-ev and 3.5-ev band were, respectively, about ⅓ and 1/15 the intensities of these bands at the surface. However, for the crystal heated for 50 minutes, the intensities of both bands

FIG. 1. Spectra taken under x-irradiation. The dashed curve was taken from the crystal before heat treatment. The solid curve was taken after the crystal was heated at about 870°K for 15 minutes.
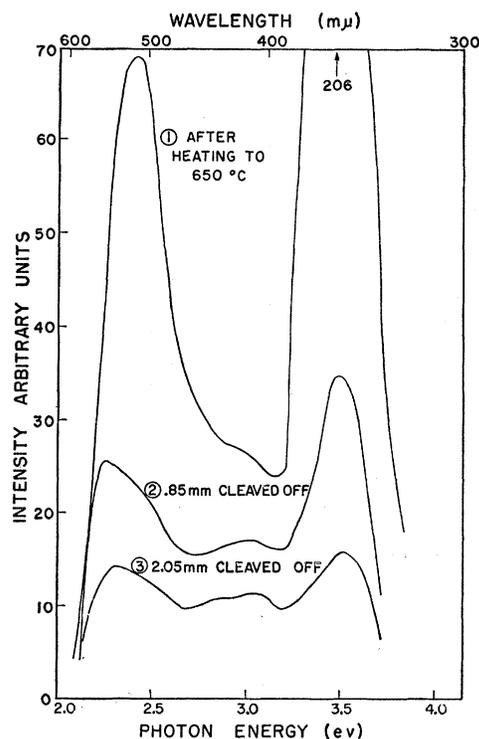
FIG. 3. Spectra of a heated crystal as a function of depth into the crystal. Curve 1 taken from original surface, Curve 2 after cleaving 0.85 mm off, and Curve 3 after cleaving 2.05 mm off.

were only a factor of two less than their respective intensities at the surface. The intensities at the surface were roughly equal for each heating time. These results are qualitatively consistent with the formation of luminescence centers at the surface of the crystal followed by their diffusion into the interior of the crystal.

With the above results in mind, the role of the atmosphere surrounding the crystal was investigated. It was found that essentially the same results were obtained whether the crystals were heated in air or in vacuum down to 10^{-5} mm of Hg. However, if the crystals were heated in the presence of sodium vapor, the intensities at 2.45 and 3.51 ev were only about 1/20 that of a crystal given the same treatment in air.

The effect of heating could be greatly reduced and modified by prolonged x-irradiation. An example of this effect is given in Fig. 4. Curves 1 and 2 indicate the changes brought about in the spectra of Fig. 1 by prolonged x-irradiation. As shown, the effect of such treatment is to decrease gradually the intensity of the 3.51-ev and 2.45-ev bands until the spectrum is almost identical to that before the heat treatment. The principle difference is the apparent growth of the band at 2.9 ev. The long x-irradiation was followed by a second heat treatment. As shown by curve 2 of Fig. 4, essentially the same spectrum was obtained following this treatment as following the first heat treatment. In

unheated crystals, essentially no changes were brought about by long x-irradiation.

II. Optically Induced Luminescence and Afterglow Measurements

Because of the high energy of x-ray photons, they may give rise to any number of luminescence mechanisms. However, if experiments may be devised involving low-energy photons, the number of possible mechanisms may be reduced. An obvious way to do this was to excite F-center electrons into the conduction band[12] and to look for luminescence produced when these electrons fall into lower lying states. To do this, crystals were first colored by x-irradiation and then irradiated with light absorbed in the F band and examined for luminescence at other wavelengths.

Because of the difficulty in separating the exciting and excited light, it was impossible to examine the entire spectral region at once. Rather, the regions from 2.1 ev to 2.7 ev and that from 3.0 ev to 5.0 ev were studied separately. For the former range, the F-light was provided by the 2.84-ev line of an H-4 mercury arc. For the shorter wavelength range, the 2.58-ev line from a zinc arc was used.

The results obtained from heat-treated crystals are given in Fig. 5. The bands found under x-irradiation at about 3.5 ev and 2.45 ev are present. Thus, both of these bands appear to result from electronic transitions from the conduction band to lower lying levels. The intensities of the two bands in Fig. 5 should not be compared since the intensity of the exciting light was different in the two cases. The 5.0-ev band was not
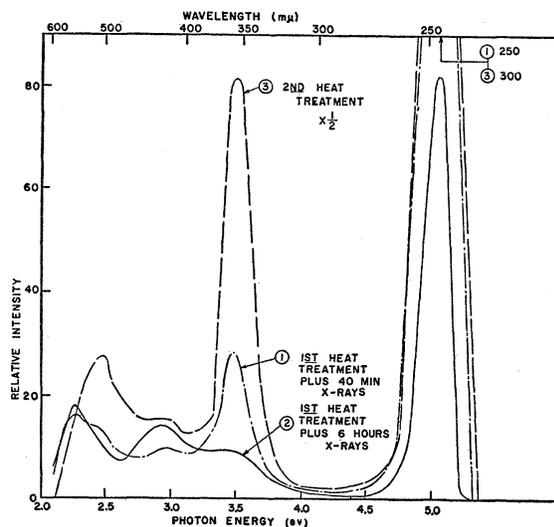
FIG. 4. The changes brought about in the spectrum (after heat treatment) of Fig. 1 by prolonged x-irradiation are shown by curves 1 and 2. Curve 3 indicated the effect of a second heat treatment.

[12] R. W. Pohl, Proc. Phys. Soc. (London) 49, 3 (1937), extra part.

found. It is possible that this was due to the lack of sensitivity of the detection equipment in that spectral region. Also shown for reference in Fig. 5 are Pick's[13] curves for the F and F' absorption bands in NaCl.

No optically induced luminescence was obtained from crystals which had not been heat-treated. Comparison of the x-ray-induced luminescence intensities from heated and unheated crystals with the optically induced luminescence from heated crystals indicated that the apparatus may have been too insensitive for the detection of such luminescence. All the data given below for optically induced luminescence and afterglow refer to heat-treated crystals.

The optically induced luminescence at 3.5 ev was studied as a function of time of F-irradiation, and typical results are shown in Fig. 6. During the periods marked "arc on," the crystal was irradiated with F-light. During the other periods, a shutter was placed between the arc and crystal. The optical luminescence was characterized by an initial rapid decrease in luminescence intensity followed by a region of slowly decreasing intensity. If a crystal was left in the dark for a period of time following an irradiation and then irradiated once more, the initial intensity was greater than that at the end of the previous irradiation; but the intensity again decreased swiftly and reached a slowly decreasing value. The amount of revival was found to increase with the time the crystal was left in the dark. In taking optically induced spectra, care was taken that the results were not altered by these effects.

An afterglow was observed following x-irradiation
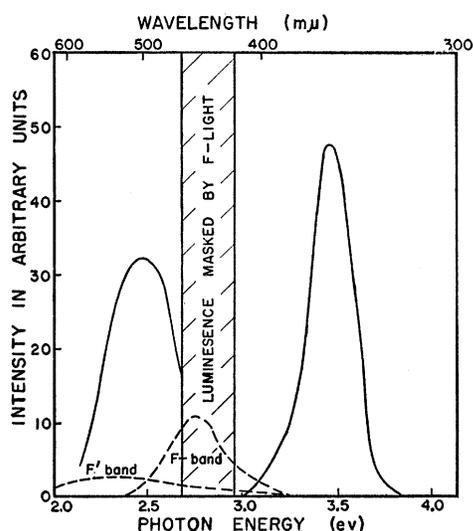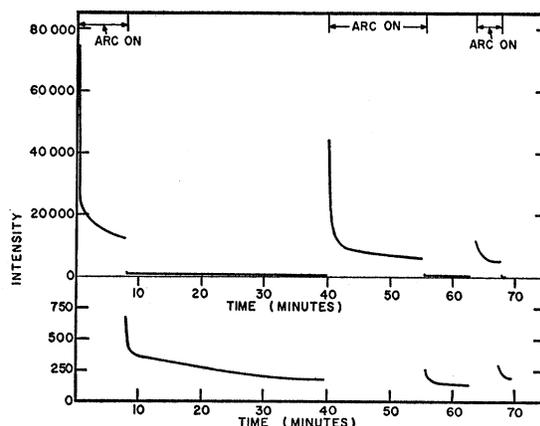
FIG. 6. Optically induced luminescence at 3.5 ev as a function of time. The crystal was only exposed to F-light during the periods marked "arc on." The afterglow observed between F-irradiations is plotted on an expanded scale.

which persisted for a number of hours.[14] The spectrum of this afterglow was obtained and, except that no 5.0-ev band was observed, was found to be essentially the same as that observed under continuous x-irradiation with bands at 2.45 ev and 3.5 ev and a less significant band at about 3.0 ev.

Figure 7 shows the decay of the 2.45- and 3.5-ev afterglow bands. The two luminescence bands seem to decay in parallel manner. If these curves are divided into straight line portions (a questionable procedure due to the scatter of points), half-lives for electrons in traps, decreasing from 7 to 110 minutes, are indicated. A striking feature of the decay curve is the persistence of the afterglow. Note that it is still measurable after almost 8 hours.

After the afterglow had decayed to a low level, it could be revived by a short irradiation with light absorbed in the F-band (F-light), see Fig. 7. This was accompanied by a change in the relative intensity of the 3.5-ev and 2.45-ev bands (the 2.45-ev band being stronger than the 3.5-ev band following the F-irradiation), but with no other marked change in the luminescence spectrum. Assuming that the afterglow is due to the thermal ionization of traps, this revival may be explained as a refilling of traps by electrons excited into the conduction band by the F-light. Following the F-irradiation, the luminescence intensity had a very fast initial decay and then leveled off to a slower decay after about 14 minutes.

It is conceivable that the trapping centers may be F' centers. For additively colored NaCl at room temperature, Pick[13] found a half-life of about eight minutes for such centers. However, as the numbers of F' centers becomes small compared with the number of F centers, retrapping of electrons at F centers would become more

FIG. 5. Spectrum of the luminescence induced in the region 2.1 ev to 2.7 ev by irradiating an x-ray-colored crystal with F-light. Spectrum of the luminescence induced in the region 3.0 to 5.0 ev by irradiating an x-ray-colored crystal with F-light. The detector sensitivity was quite poor in the region below 4.5 ev.

[13] H. Pick, Ann. Physik 31, 365 (1938).

[14] In Fig. 6 the intensity of the afterglow at 3.5 ev is shown for the periods when the crystal was in the dark. The afterglow intensity is plotted on an enlarged scale below the principal curves.
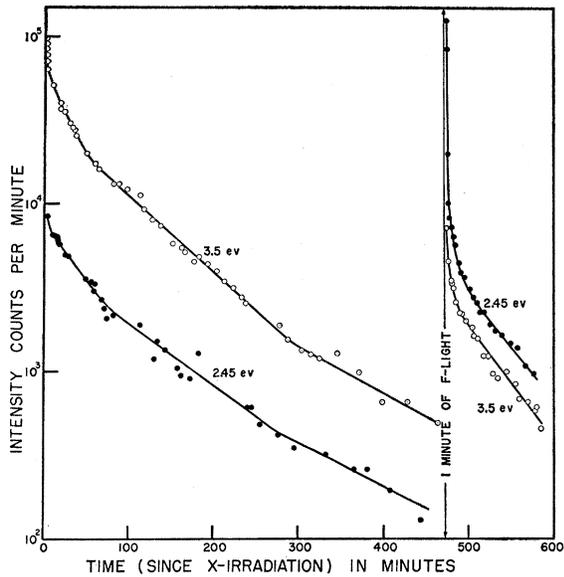
FIG. 7. The afterglow at 2.45 ev and 3.5 ev as a function of time. After decaying for 472 minutes, the crystal was irradiated for 1 minute with F-light.

likely thus increasing the time an electron would spend in F' centers. One would thus expect that the measured half-life of the F' centers would increase with time; however, it is not at all evident that they should increase in discrete steps.

With the equipment at hand, there were two methods by which the influence of F' centers might be investigated. The first was to irradiate the crystal with light of a fixed energy lying in the F' band. If F' centers were responsible for the afterglow, such irradiation should remove electrons from F' centers into the conduction band; thus inducing luminescence under the irradiation and a reduced afterglow following irradiation. The extreme width of the F' band (see Fig. 5) makes the data obtained by this method somewhat inconclusive. The second method was to study the efficiency of light in the spectral region from 0.9 ev to 2.6 ev in inducing luminescence. The luminescence induced by light of a certain energy presumably would be proportional to the absorption of that light and thus would indicate the position of the trapping centers.

Figure 8 shows data obtained by the first method. On the ordinate is the logarithm of luminescence intensity at 2.45 and 3.5 ev (in arbitrary units) plotted *versus* the time (in minutes) since x-irradiation. For the first 39 minutes following x-irradiation, the afterglow was followed. Then the crystal was irradiated for two minutes with light which fell in the F' band at 1.63 ev. Such irradiation induced a luminescence which was initially about 100 times stronger than the afterglow but which decreased by a factor of about 20 in two minutes. This F' irradiation resulted in a decrease in the afterglow by about the same factor of 20. A second irradiation with the 1.63-ev light again induced a

relatively strong luminescence which decreased much slower under the irradiation. This irradiation resulted in a much smaller reduction in the 3.5-ev afterglow than the first F-irradiation and in an initial increase in the 2.45-ev band. The reduced quenching effect of the second 1.63-ev irradiation may have been due to a very slight amount of F-band absorption at 1.63 ev.

Following the third series of afterglow measurements, the crystal was irradiated with F-light for one minute. This had the usual effect of increasing the afterglow by several orders of magnitude and reversing the relative intensities of the 2.45-ev and 3.5-ev bands (the luminescence induced by the F-light was too intense to be detected by the apparatus used for this experiment). In other experiments, it was found that the effects described here could also be produced if 1.95-ev light was used instead of the 1.63-ev light.

The type of experiment described above suffers from the fact that it gives information only about the effect of light of one energy on the trapping states. Since the F' band is so broad, it would not have been practical to perform similar experiments all along this band. Rather, experiments designed to determine the efficiency of light of energy between 0.9 and 2.6 ev in inducing luminescence were performed.

The curves given in Figs. 9 and 10 were obtained by going in approximately 0.1-ev steps from lower to higher energies. On the ordinate is plotted the logarithm of the luminescence induced per exciting photon (in arbitrary units). The photon energy of the exciting light is given on the abscissa. Curve 1 of Fig. 10 was taken 6.5 minutes after the crystal had been x-irradiated. The afterglow was 12 800 counts/min just before the curve was taken. After curve 1 was taken, the crystal was left in the dark for twelve hours allowing the afterglow to decay to less than 100 counts/min; then
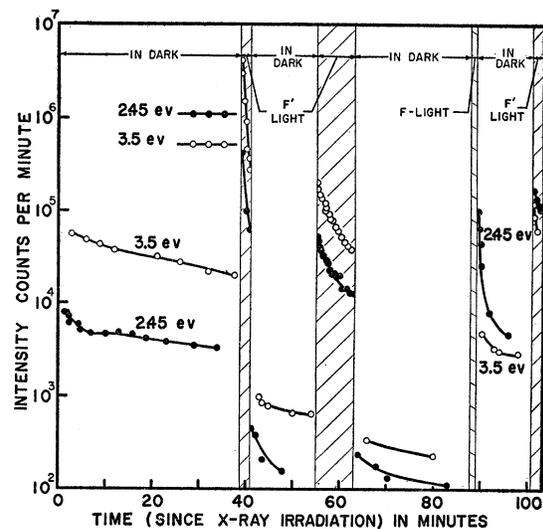
FIG. 8. The effect of F and F' light on the afterglow. The crystal was irradiated with F'-light during the periods marked "F'" and by F-light during the period marked "F."

curve 2 was taken. There is a large difference between curve 1 and curve 2 in the region 1.1 to 2.3 ev. This is assumed to indicate the position of the trapping centers which were depleted as the afterglow decayed away. The rise starting at about 2.0 ev in curve 2 is probably due to the F band absorption. The luminescence rises only slowly after 2.3 ev because of the sharp decrease in the luminescence induced by F-light with time of F-irradiation as shown in Fig. 7.

After curve 2 was taken, the crystal was irradiated with F-light for five minutes raising the afterglow intensity to 1000 counts/min and curve 3 was taken. The increase in the induced luminescence from 1.2 to 2.0 ev over that of curve 2 is apparent. This increase is about what would be expected owing to creation of F' centers by the F-irradiation. After curve 3 was taken, the crystal was left in the dark for two and a half hours, after which time the afterglow had again decayed to less than 100 counts/min. Then curve 4 was taken. Comparison of curves 3 and 4 indicates the disappearance of the band from 1.2 to 2.0 ev. Again, this accompanies the disappearance of the afterglow.

The shapes of curves 2 and 4 of Fig. 9 indicate that a band having a long half-life might be present at 1.3 ev. To test for this the curves of Fig. 10 were taken. An x-irradiated crystal was left in the dark for 36 hours and then curve 1 of Fig. 10 was taken. There was, of course,

FIG. 10. Efficiency of light of energy between 0.9 ev and 2.6 ev in inducing 3.5-ev luminescence. Curve 1 was taken from a crystal left in the dark for 36 hours after x-irradiation (no measurable afterglow). Curve 2 was taken after F-irradiation (raising afterglow to 400 counts/min).

no measurable afterglow before this curve was taken and no band at 1.3 ev is evident in curve 1. The effect of three minutes of F-light (raising the afterglow to 400 counts/min) is shown in curve 2. The usual effect attributed to F' absorption is present in addition to the appearance of a band at 1.3 ev. This seems to verify the presence of a band at 1.3 ev having a very long lifetime and contributing only slightly to the afterglow.

These measurements are rather crude (particularly because the spectra must be swept out swiftly in order to minimize bleaching of centers by the exciting light). However, it seems quite possible that the F' band plays an important role in the afterglow. A slowly decaying band at about 1.3 ev may also be present.

CONCLUSIONS

For the non-heat-treated crystals, there is nothing here which would allow determination of the mechanism giving rise to the x-ray-induced luminescence. However, for the heat-treated crystals, the production of the 2.45- and 3.5-ev bands by F-irradiation of x-ray-colored crystals indicate that these bands are due to electronic transitions from the conduction band to lower lying levels. Since the 2.45- and 3.5-ev bands were also the principal bands present in the afterglow spectra and (excluding the 5.0-ev band) in the x-ray-induced spectra of the heat treated crystals, it is assumed that in both of these cases the 2.45- and 3.5-ev bands result

FIG. 9. Efficiency of light of energy between 0.9 and 2.6 ev in inducing 3.5-ev luminescence. Curve 1 was taken 6½ minutes after x-irradiation (afterglow—12 800 counts/min). Curve 2 was taken 12 hours later (afterglow—less than 100 counts/min); then the crystal was subjected to 5 minutes of F-irradiation (afterglow—1000 counts/min) and curve 3 taken. Curve 4 was taken after the crystal was left for an additional 2½ hours (afterglow less than 100 counts/min).

from electronic transitions from the conduction band into lower lying states. The centers creating these states cannot be positively identified; however, the data concerning their formation will be briefly discussed and a guess will be ventured as to their nature.

The results reported here seem to indicate that the luminescence centers responsible for the 3.5- and 2.45-ev bands are produced at the surfaces of the crystals and diffuse into the crystal during the heat treatment. It is hard to see how luminescence centers due to foreign impurities already in the crystal could be activated in such a manner. There are also indications that the luminescence centers are not formed by atmospheric molecules diffusing into the crystal. First, essentially similar results were obtained from crystals heated at atmospheric pressure and at pressures of 10^{-5} to 10^{-3} mm of Hg; and, secondly, there is no similarity between the spectra found here and those obtained by Honrath[15] after adding atmospheric gases to NaCl.

The manner of production of luminescence centers reported here is consistent with the removal of sodium atoms at the surface of the crystal. This hypothesis is supported by the fact that the 2.45- and 3.5-ev bands did not appear in crystals heated in an atmosphere of sodium vapor. Removal of sodium atoms would leave V-type centers. Since V_1 centers are unstable at room temperature[1] and since V_3 centers have a negative charge associated with them, only V_2 and V_4 centers will be considered here as possible luminescence centers.

Because of the reversal in the relative intensities of the 3.5- and 2.45-ev afterglow bands following F-irradiation, the 3.5-ev luminescence will be associated with the V_2 center and the 2.45-ev with V_4 centers. The reasoning behind this is as follows: during F-irradiation, V_2 centers will capture electrons, reducing the number of these centers and forming V_3 centers having a negative charge. The freeing of electrons from F centers would leave halogen ion vacancies. The V_3 centers and halogen ion vacancies would be attracted together, forming V_4 centers. Thus, the number of V_2 centers would be reduced relative to the number of V_4 centers by the F-irradiation.

If the luminescence were due to electrons falling into V_2 and V_4 centers, the sum of the absorption energies for these bands and luminescence energies should be approximately equal to the band-to-band energy. This band-to-band energy is not well known but probably lies between 8.2 and 9.5 ev.[16] The sum of the V_2 absorption energy[17] and 3.5-ev luminescence energy is 9.1 ev which is in the right range. This model would then predict a V_4 absorption energy of about 6.6 ev.

One flaw in this model is the fact that V_2 and V_4 centers are produced by x-irradiation and thus luminescence associated with them, if present, should be observable in non-heat-treated crystals; however, it may be that the V centers are not present in large enough quantities in these crystals to contribute strongly to the luminescence. It should be noted that the shapes of the spectra from unheat-treated crystals suggest that unresolved bands may be present at 2.45 and 3.5 ev. In any case, this identification of the luminescence centers must remain completely in the realm of speculation until and unless it is verified directly. This might be done by absorption measurements. Although these arguments have been made assuming that the V centers were the luminescence centers, they would hold for any set of centers having properties similar to V centers.

The change in the spectra from heat-treated crystals after prolonged x-irradiation is possibly due to a coagulation of the luminescence centers brought about by the x-irradiation. The predominance of the 2.9-ev band after the heavy x-ray dosage indicates that this band may be associated with some configuration of coagulated centers.

The afterglow seems to be a bimolecular process involving the ejection of electrons from traps into the conduction band through which they wander until falling into the luminescence centers. It has been shown that the number of electrons in the traps may be reduced by irradiating the crystal with light absorbed in the near infrared and that the afterglow may be revived by irradiation with F-light. F' centers are probably the most important of these traps; however, one with a very slow decay at 1.3 ev may also be present.

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[16] Hartman, Nelson, and Siegfried, Phys. Rev. **105**, 123 (1957).

[17] Casler, Pringsheim, and Yuster, J. Chem. Phys. **18**, 1564 (1950).