

Symmetry of the Green Phosphorescence of Heat Pretreated Colored KCl Crystals

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On thermal pretreatment in the open air (at 700°C), the phosphorescence of KCl crystals after α coloring at liquid-air temperature turned from violet to green. While the former phosphorescence showed no anisotropy the green was found to become partially polarized after irradiation with [011] light. The irradiation also induced dichroic absorption at 3650Å. Both the polarization in the phosphorescence and the dichroic absorption persisted up to nearly 200°K.

The polarized light bleached the component of the 3650Å absorption in parallel to it, but enhanced the green phosphorescence with the main effect on the perpendicular component.

It is suggested that oxygen which diffused into the crystal during the heat treatment is responsible for the asymmetric center.

INTRODUCTION

THE nature of the processes involved in the emission from colored alkali-halide crystals is not yet clear. Investigation of the symmetry properties of this emission might help in establishing a model for the transitions involved. Lambe and West have found¹ that bleaching a KCl crystal with 3650Å light polarized in the [011] direction after coloration with α rays at 77°K induces anisotropy in the low-temperature phosphorescence. This polarized emission was found to persist up to about 130°K, the temperature at which the V_1 band bleaches thermally. On the other hand, the V_1 band itself did not show any dichroism, which is in accordance with the symmetrical model ascribed to it by Seitz.² Lambe and West suggested, therefore, that a center other than V_1 with an axis of symmetry along [011] and absorbing at 3650Å should be present in KCl α rayed at 77°K. Such a center was, in fact later observed experimentally,^{3,4} and was ascribed to Cl_2^- molecule ions.

It was the aim of the present work to examine in more detail the low-temperature phosphorescence of

colored KCl crystals, its symmetry properties, and its possible correlation to the Cl_2^- center.

Surprisingly enough, no anisotropy could be detected with our untreated KCl crystals. It was only after thermal pretreatment, which completely changed the spectral distribution of the phosphorescent light, that anisotropy could be induced in it. This polarized emission seems to differ, however, from that observed by Lambe and West as will be described below.

EXPERIMENTAL

The specimens used were cleaved from KCl single crystals grown by Harshaw Chemical Company to form plates approximately 8×6×1 mm in size. They were held in a vacuum cryostat designed as described previously.⁵ A heating element made it possible to warm up the crystal in the cryostat at a uniform rate from liquid-air temperature to over 600°K.

Polaroid films, selected to give good transmission down to nearly 3000Å, were used as polarizer and analyzer. They were fitted in suitable holders on either side of the cryostat, and could be manually rotated through 360°. The analyzer was fitted with stops which enabled it to be switched over with ease from one fixed position to another; e.g., from +45° from the vertical to -45° from it and *vice versa*.

The crystals were colored at liquid-air temperature by α rays (35 kvp and 14 ma). After coloring they were bleached with polarized monochromatic light. A Beckman DU monochromator with an air-cooled Xe compact arc (Hanovia 507 c, 800 w) supplied the monochromatic light.

The whole experimental setup is shown in Fig. 1. L is the light source, Q —a quartz condensing lense, DU —the monochromator, P —the polarizer, A —the analyzer, C —the crystal in the cryostat, D —the detector (IP 21 photomultiplier) and amplifier, and R —a 50 mv Brown recorder. Details of amplification were as described elsewhere.⁶

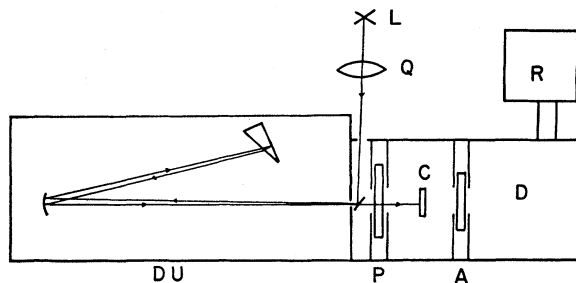


FIG. 1. Experimental setup for bleaching and for detection of the polarized emission. L —Light source, Q —quartz condensing lense, DU —the Beckman DU monochromator, A —the analyzer, P —the polarizer, C —the crystal in the cryostat, D —the detector and amplifier, and R —a 50 mv Brown recorder.

¹ J. Lambe and E. J. West, Phys. Rev. **108**, 634 (1957).

² F. Seitz, Revs. Modern Phys. **26**, 7 (1954).

³ T. G. Gastner and W. Känzig, J. Phys. Chem. Solids **3**, 178 (1957).

⁴ C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **111**, 1235 (1958).

⁵ A. A. Braner and A. Halperin, Phys. Rev. **108**, 932 (1957).

⁶ A. Halperin and A. A. Braner, Rev. Sci. Instr. **28**, 959 (1957).

The monochromator slit was suitably changed on passing from one wavelength to another so as to have the polarized bleaching light equal in intensity for all wavelengths. Calibration of slit widths was carried out for the set as a whole, taking into account the dependence on wavelength of the sensitivity of the photomultiplier. Absorption of the Polaroid was, of course, also included in the calibration.

The crystalline quartz windows in the cryostat showed optical activity, and were, therefore, replaced by windows of fused silica.

For optical bleaching the polarizer (P in Fig. 1) was fixed in parallel with either the (011) or the (010) plane of the crystal. After a fixed bleaching time the lamp was extinguished, when the phosphorescence and the thermoluminescence were recorded. During these measurements the analyzer was switched back and forth between the two positions indicated by the stoppers, one fixed in parallel with the plane of polarization of the bleaching light, and the other perpendicular to it.

Some of the bleaching experiments were carried out with a filter (Wratten 18A, maximum transmission near 3660Å) replacing the monochromator. In these experiments the detector D (Fig. 1) was removed to enable bleaching of the crystal with the filtered light from a mercury arc (MD/E , 250 w) through the analyzer A which served now as a polarizer. After the fixed bleaching time the detector was replaced when measurements were taken as before, with the polarizer functioning again as analyzer.

Measurements of spectral distribution of the weak phosphorescence at low temperature and of the thermoluminescence peaks were carried out as described elsewhere.⁷

Absorption measurements were made with a Beckman DK spectrophotometer. Two Polaroid films were fitted in two of the holes of the filter slide near the exit slit of the DK monochromator. One of these Polaroids was fixed parallel and the other perpendicular to the plane of polarization of the bleaching light, so that the trans-

mission of the crystal could be recorded with light polarized in either of the two orientations.

RESULTS

(1) Polarization of the Phosphorescence

Attempts to reproduce the results of Lambe and West¹ were unsuccessful. In some crystals the phosphorescence at liquid air temperature could hardly be detected. In others, which showed phosphorescence, the polarized bleaching light did not induce any anisotropy in the phosphorescence.

Earlier work in this laboratory⁷ showed that thermal pretreatment affects the spectral distribution of the low temperature phosphorescence in KCl. The failure in the attempts to induce polarization in the phosphorescence was, therefore, attributed to differences in the emitted light.

The thermal pretreatment experiments were successful. Preheating the crystal for 2 hours at about 700°C changed the phosphorescence of the crystals. They then showed polarization of the emitted light after bleaching with polarized light. It will be shown below that the phosphorescence of these crystals were composed mainly of a green emission band (about 5200Å), instead of the violet one (~ 4000 Å), which was the main band in the untreated crystals. Figure 2 shows a typical run. The intensity of the phosphorescence shortly after x raying the crystal is shown at the left side of the figure. The crystal was then bleached for 30 min with monochromatic light (3600Å) polarized along the $[011]$ crystal direction. The phosphorescence after bleaching was now measured with the analyzer switched over back and forth between $[011]$ and $[0\bar{1}1]$ directions (the corresponding portions on the curve are indicated by \parallel and \perp in the figure). After measuring the partially polarized phosphorescence for a few minutes, the heating coil in the cryostat was turned on, and the glow was recorded, again with the analyzer switched in parallel and perpendicular to $[011]$ at intervals.

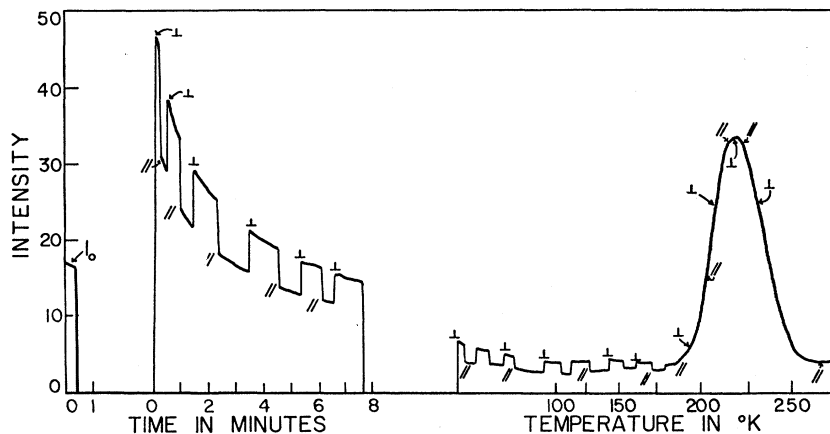


FIG. 2. The polarization in the emission from x -colored KCl crystal bleached with $[011]$ polarized light. \parallel indicates the intensity in $[011]$, and \perp in $[0\bar{1}1]$ direction.

⁷ A. Halperin and N. Kristianpoller, J. Opt. Soc. Am. 48, 996 (1958).

The results can be summarized:

- Bleaching induced negative polarization⁸ in the phosphorescence.
- The bleaching *increased* the phosphorescence intensity both in the parallel and perpendicular directions.
- The phosphorescence added by the bleaching light seems to decay faster than that present before bleaching.
- The anisotropy persists to nearly 200°K, when a strong glow starts.
- No anisotropy was found in the thermoluminescence, neither at about 200°K nor at higher temperatures (not shown in Fig. 2).

The effect of wavelength of polarizing light on the polarization of the phosphorescence is shown in Fig. 3. Wavelengths around 3600Å are shown to be most effective in inducing the anisotropy. For a given wavelength the polarization depended on the intensity of the bleaching light and on bleaching time, but became saturated on prolonged bleaching. Polarizations of about 20% were obtained at saturation in our experiments. Care has been taken, in the set of measurements for the curve in Fig. 3, not to approach saturation, which might have masked the effect of different wavelengths.

The enhancement in the phosphorescence by the bleaching light was obtained from the same set of measurements. Figure 4 shows the dependence of this enhancement on wavelength. The ordinate gives the ratio of the perpendicular component of the phosphorescence intensity after bleaching (I_{\perp}) to that before bleaching (I_0). Again we have the strongest effect at

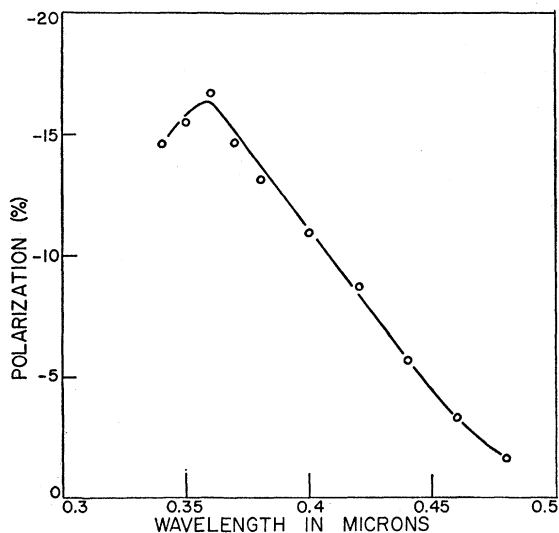


FIG. 3. The effect of wavelength of the bleaching light on the polarization of the phosphorescence.

⁸ Polarization is defined as $P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$, where I_{\parallel} and I_{\perp} are the intensities of the light emitted parallel and perpendicular to the direction of the bleaching light, respectively.

about the same wavelength as in Fig. 3. It should be noted that no correction has been made for the self decay in the phosphorescence which would have taken place during the bleaching time (30 min in these experiments).

(2) Spectral Distribution of the Phosphorescence

The spectrum of the phosphorescence of our untreated crystals is shown in Fig. 5, curve *a*. It peaks at about 3900Å. The phosphorescence of the same crystal after pretreatment for two hours at about 700°C in the open air is given by curve *b*. There is still a very weak component at 3900Å. The main band, however, appears now at 5200Å. The band at 5200Å proved necessary for obtaining anisotropy in the phosphorescence in our crystals; crystals showing a stronger green phosphorescence showed also more pronounced anisotropy. Further bleaching with polarized light (3660Å) was found to effect mainly the green component. This is shown in Fig. 6, where curve *a* corresponds to the crystal just after x raying, and curve *b* was obtained after bleaching with [011] polarized light. There is some decrease in the intensity of the violet band, while the green band was considerably enhanced by the bleaching light. The bleaching light also caused a reduction in the intensity of the thermoluminescence.

(3) The Optical Absorption Bands

The x-ray coloration of the heat treated crystals differs entirely from that of the untreated ones.⁹ The absorption spectrum of a colored heat treated KCl

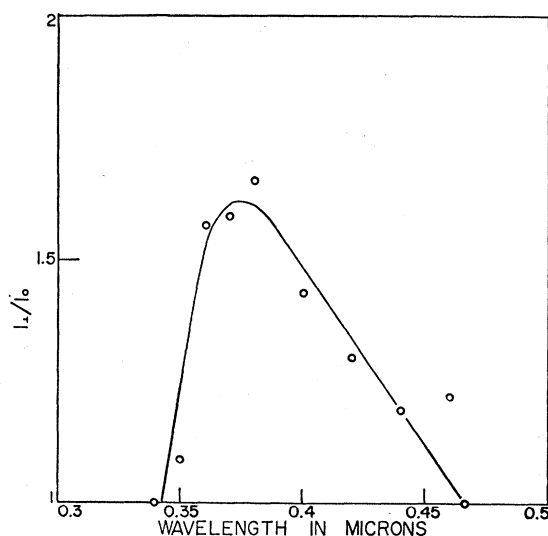
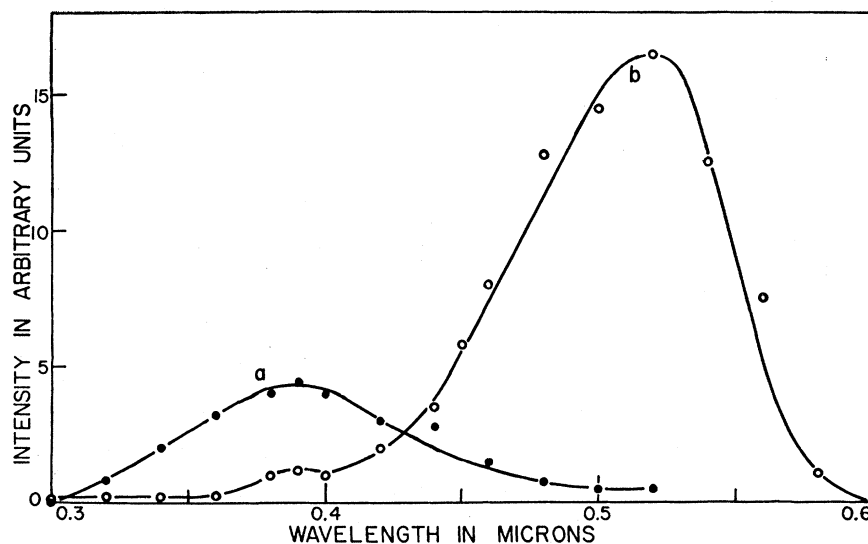


FIG. 4. The dependence of the enhancement of the phosphorescence on the wavelength of the bleaching light. I_0 is the intensity of the [011] component of the phosphorescence after x coloration, I_{\perp} —that after bleaching with [011] light.

⁹ A. Halperin and M. Schlesinger, J. Chem. Phys. **30**, 339 (1959).

FIG. 5. The spectral composition of the phosphorescence of an x -colored KCl crystal. a —before heat treatment, b —after heat treatment.



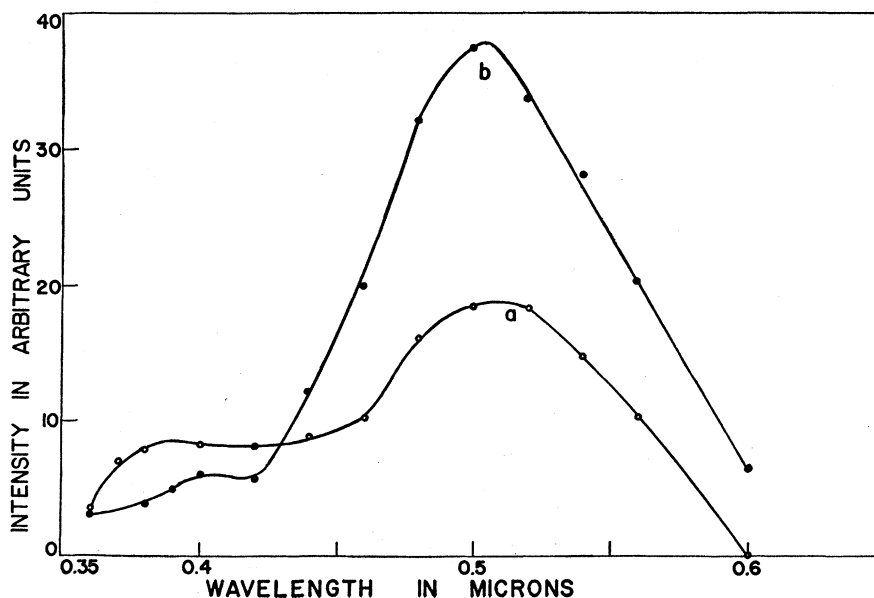
crystal, whose phosphorescence was described in the preceding paragraph (Fig. 5, curve b), is shown in Fig. 7. Curve a was measured just after x raying and it is shown on a reduced scale to the right of Fig. 7. The absorption was the same whether taken with $[011]$ or $[0\bar{1}1]$ polarized light. The spectrum consists of a main absorption band at about 4200Å with a shoulder towards shorter wavelengths. The F band (at about 5400Å) is hardly apparent. Bleaching (20 min) with $[011]$ polarized light (3600Å, filtered) caused a reduction in the 4200Å band, which was equal with $[011]$ and $[0\bar{1}1]$ light. In the shoulder at about 3600Å, however, the bleaching induced some dichroism. This is shown in Fig. 7 curves b and c taken with $[011]$ and $[0\bar{1}1]$ polarized light, respectively. The difference between curves c and b

(Fig. 8) fits well the curve obtained by Delbecq et al.⁴ for doped KCl crystals, which was ascribed to the Cl_2^- center.

The thermal stability of the absorption bands was also examined. The results are given in Fig. 9, in which curve a gives the thermal bleaching at 4200Å and curve b —that at 3600Å.

At first sight it appears as if the 3600Å band bleaches only partly at about 210°K, while most of it remains stable till about 360°K. Detailed inspection of the spectrum, however, shows that the 3600Å band bleaches completely at the lower temperature range, while the sharp drop at 360°K is entirely due to the disappearance of both, the band at 4200Å, and another weak band at 3350Å. The latter is completely covered by the 3600Å

FIG. 6. The spectral composition of the phosphorescence of a heat-pretreated x -colored KCl crystal. a —after x -coloration, b —after bleaching with $[001]$ light (360 mμ) for 15 minutes.



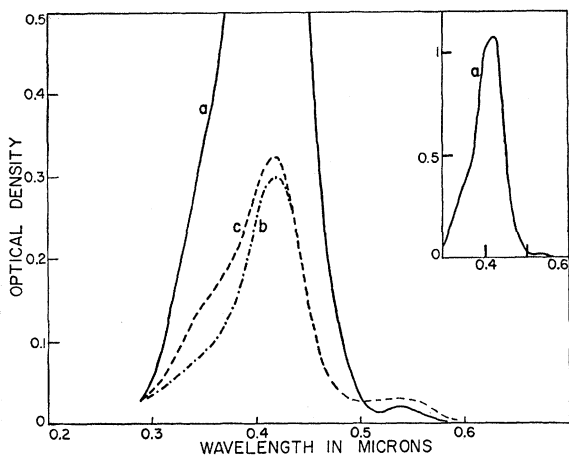


FIG. 7. Absorption spectra of a heat-pretreated x -colored KCl crystal. a —after x coloring (taken with either [011] or [011] light), b and c taken after bleaching with [011] light (360 $m\mu$) for 20 minutes. b —taken with [011] light, c —with [011] light.

band at temperatures below 210°K, but can be seen above this temperature, when the former bleaches away.

DISCUSSION

The center responsible for the asymmetry in the green phosphorescence is certainly not the V_1 center, which was shown by Lambe and West¹ to be symmetrical. Lambe and West encountered some difficulty trying to explain the equal thermal stabilities of the asymmetrical phosphorescence and the V_1 center. This was not the case with the phosphorescence of our heat treated crystals, which showed higher thermal stability, and differed also in spectral distribution from that of the V_1 glow at 130°K. It is of interest that a green thermal glow peak was observed⁷ in KCl crystals slightly below 200°K, which is just the temperature at which the asymmetry in the green phosphorescence disappears.

We have repeated many times, and with different crystals, our attempts to induce anisotropy in the violet phosphorescence present in our untreated crystals. All the efforts were, however, unsuccessful, and it is not clear why Lambe and West succeeded in this point. A possible explanation might be that the phosphorescence in their untreated crystals was different from that in ours. Unfortunately Lambe and West did not measure the spectrum of the weak phosphorescence in their crystals.

Our results seem to be rather similar to those reported by Lambe and West for thallium activated KCl crystals. Not only the thermal stabilities of the polarized phosphorescence were similar, but it seems also that the spectral bands of the phosphorescence were the same in both cases.

The optical absorption of our colored crystals (Fig. 7) was very similar to that obtained by Delbecq et al.⁴ for silver activated KCl crystals. In addition, the di-

chromism induced in the 3600Å absorption band, as it appears in our subtraction curve (Fig. 8), follows closely the one obtained by Delbecq et al. for their metal doped crystals (reference 4, Fig. 5).

These authors attributed the asymmetry in the absorption band to Cl_2^- centers. It is, however, difficult to explain the higher thermal stability of the centers in the doped crystals unless we assume some proximity between the Cl_2^- ions and the metal impurities. Were this the case it would be still more difficult to explain how the introduction of oxygen by the heat treatment resulted in just the same spectral band, and just the same thermal stability of the Cl_2^- center as the doping of the crystal with thallium, lead, or silver.

It is worth noting at this point that oxygen was shown by several investigators to induce long wavelength luminescence in alkali-halide crystals. Honrath¹⁰ has shown that alkali halide crystals heat treated in oxygen luminesce on irradiation with ultraviolet light. This emission showed a band structure extending from the blue to longer wavelengths, with maximum intensity in the green. Although we did not observe such a structure in our green phosphorescence this might have been due to experimental limitations, viz., the wide monochromator slits (2 mm, 500Å spectral half width at 5500Å) used to measure the spectrum of the weak phosphorescence, and the steep drop in the sensitivity of our photomultiplier (RCA IP28) at longer wavelengths beyond the green.¹¹

Honrath attributed this long wavelength emission, which was shown to be nearly the same for all alkali halides, to an isolated center like ClO_4 . Ewles and Barmby,¹² who also investigated the oxygen induced luminescence in alkali halides, came to the conclusion that it must be due to the oxygen itself. Otherwise, they argue, it would be difficult to explain how the replace-

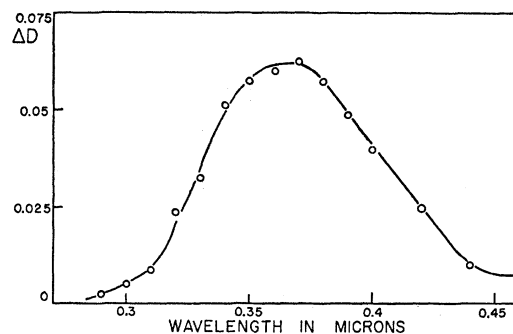


FIG. 8. Subtraction curve, showing the difference between curve c and b in Fig. 7.

¹⁰ W. Honrath, Ann. phys. **529**, 421 (1937).

¹¹ More accurate spectral measurements being carried out now in this laboratory, show that the green phosphorescence possesses indeed a band structure.

¹² J. Ewles and D. S. Barmby, Proc. Phys. Soc. (London) **B69**, 670 (1956).

ment of the chlorine atom in the center by another halide does not change the separation between the emission bands. These authors suggest that O_2^+ ions should be responsible for the long wavelength emission.

Recently Känzig and Cohen¹³ reported observations of paramagnetic resonance spectra of alkali halide crystals heat treated in an oxygen atmosphere. They came to the conclusion that the centers induced by the treatment are O_2^- ions. Their observations indicated that the O_2^- center is oriented in $[011]$, and they have suggested that the long wavelength luminescence observed by Honrath¹⁰ and by Ewles and Barmby¹² might be associated with the O_2^- centers. Our asymmetric centers seem also to be associated with the long wavelength emission. However, they cannot be identified with the O_2^- centers for the latter are stable even above room temperature.¹⁴ It is also difficult to identify the asymmetric centers in our heat treated crystals with Cl_2^- which differ in thermal stability. In addition, the Cl_2^- absorption band in pure KCl crystals seems to differ towards the longer wavelengths from our subtraction curve (Fig. 7). This curve fitted well those given by Delbecq et al.,⁴ but it did not fit the Cl_2^- absorption curve given by Lambe and West for pure KCl (reference 1, Fig. 3) so well.

It cannot be decided from our experiments what the exact nature of the asymmetric centers induced by heat treatment is. It should, however, be associated in some way with oxygen. The similarity in behavior between these centers and those obtained with metal doped crystals^{1,4} might then be attributed to oxygen that penetrated in some way into the metal doped crystals. One cannot, however, speculate more in this point, and

¹³ W. Känzig and M. H. Cohen, Phys. Rev. Letters, **3**, 509 (1959).

¹⁴ W. Känzig (private communication).

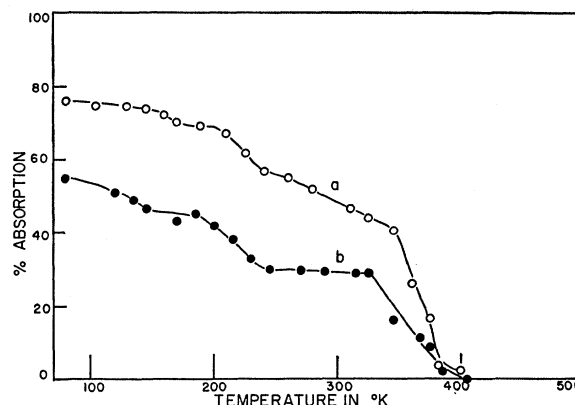


FIG. 9. Thermal bleaching curves for the absorption bands in heat pretreated x -colored KCl. a —at 420 $m\mu$, b —at 360 $m\mu$.

only very careful growing methods might give the right answer.

Another point in our results remains difficult to explain. The polarized bleaching resulted in a reduction in intensity of the thermoluminescence glow peaks, and of the violet phosphorescence. This can be explained by the release of trapped carriers responsible for both the glow and violet phosphorescence. Assuming that some of these carriers were transferred into levels, involved in the transitions responsible for the green phosphorescence, one expects an increase in the green phosphorescence, as was found experimentally. If this were the case, however, the component of the phosphorescence polarized in parallel with the bleaching light should have been the stronger in contrary to our experimental results (Fig. 2). It seems, therefore, that the transitions affected by the bleaching light are more complicated and involve more energy levels in the forbidden gap of the crystal.