PHYSICAL REVIEW VOLUME 116, NUMBER 5 DECEMBER 1, 1959

Thermoluminescence of X-Ray Colored NaCl Crystals

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(Received June 23, 1959)

Glow curves and thermoluminescence spectra taken at various temperatures during the glow have been recorded simultaneously. Spectra were obtained with a rapid-scanning spectrophotometer using a liquid-air cooled photomultiplier in conjunction with a cathode-ray oscilloscope. Peaks of the same wavelength were found to be repeated several times in the temperature range of 80–600°K.

Thermal pretreatment was found to enhance the various glow peaks by factors of a few thousands. On prolonged heat treatment the peaks above room temperature were found to decrease in intensity, while those at lower temperatures continue to grow even after 80 hours of heat treatment at 550°C.

Essentially the same results were obtained for both natural (Dead Sea) crystals and artificial ones.

INTRODUCTION

The thermoluminescence of KCl single crystals has been investigated recently in this laboratory. In some of the results already published the glow curves were shown to be composed of a complexity of glow peaks.[1] The intensity of these peaks was found[2] to be very sensitive to thermal pretreatment. The spectral distribution of the light emitted at each of the glow peaks has also been examined,[3] when peaks with the same spectral distribution were found to appear repeatedly in the glow curve.

The present paper deals with the thermoluminescence of NaCl crystals, including measurements of the spectral distribution and effects of thermal pretreatment.

In addition to synthetic crystals examinations were carried out also on natural rocksalt crystals from Sodom mountain near the Dead Sea. The similarity in the results obtained with the synthetic crystals to those obtained with the natural ones is of special interest.

Another point of interest is in the thermoluminescence spectra. It has been claimed recently by Bonfiglioli *et al.*[4] that the light emitted at each peak in the glow curve of NaCl has its own wavelength. Moreover, this assumption was basic in a model for the thermoluminescence proposed by the mentioned authors. This, however, seemed not to fit our results on KCl crystals.[3] It will be shown that similar results are obtained with NaCl crystals, where again peaks which emit the same wavelength are repeated at more than one temperature in the glow curve.

EXPERIMENTAL

The technique was essentially the same as already described previously,[1–3,5] with the exception of the following improvement:

The output from the liquid-air cooled photomultiplier (*M* in Fig. 1) was now connected after amplification to the *Y* terminals of a dc coupled cathode-ray oscilloscope (Dumont 333*R*), the *x*-beam of which was synchronized with the wavelength scanning mechanism of a Beckman *DU* monochromator. Spectra were taken photographically and wavelength calibration was obtained by taking the spectrum of a mercury lamp before and after each set of measurements.

Scanning times of only two seconds were adopted to scan the spectral range of 3000–6000 A. Some measurements were taken down to 2200 A but nothing was detected below 3000 A. Using a load resistor of 10^9 ohms in the output circuit of the photomultiplier, the time constant of the signal on the oscilloscope was about 0.06 sec. Small shifts in the spectrum due to this time lag were corrected by taking the average of two traverses of the spectrum in opposite directions.

Both the liquid-air cooled detector described above, and the conventional detector in the spectrophotometer (at A_1 in Fig. 1), which was connected to a Brown recorder, were used simultaneously. Glow curves were obtained through a quartz window on one side of the cryostat, while spectra at fixed temperatures were taken on the opposite side, where the emitted light was dispersed by the monochromator before reaching the cooled photomultiplier at *M* (Fig. 1).

Warming rates were kept at about 15 deg per min in most of the present measurements. Spectra were taken at any chosen temperature, and when needed in intervals of only 1 deg.

Exact determinations of the wavelengths of maxima were made with the slits of the monochromator closed

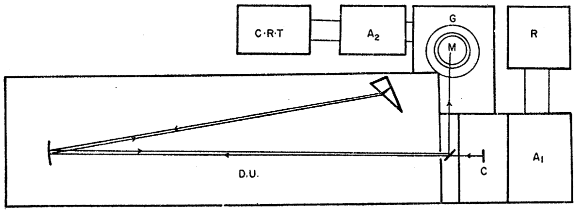

FIG. 1. Schematic diagram of the monochromator (Beckman DU), detectors and recording devices: *C*—the crystal in the cryostat, A_1—detector and amplifier, *R*—recorder for glow curves, *M*—the cooled photomultiplier, A_2—its amplifier, and *C.R.T.*—cathode-ray-oscilloscope.

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[1] Halperin, Braner, and Alexander, Phys. Rev. **108**, 928 (1957); A. A. Braner and A. Halperin, Phys. Rev. **108**, 932 (1957).

[2] A. Halperin and M. Schlesinger, Phys. Rev. **113**, 762 (1959).

[3] A. Halperin and N. Kristianpoller, J. Opt. Soc. Am. **48**, 996 (1958).

[4] Bonfiglioli, Brovetto, and Cortese, Phys. Rev. Letters **1**, 94 (1958), and Phys. Rev. **114**, 951, 956 (1959).

[5] A. Halperin and A. Braner, Rev. Sci. Instr. **28**, 959 (1957).

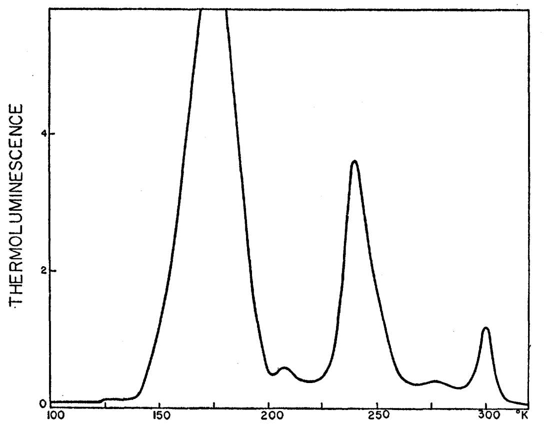

FIG. 2. Glow curve of a NaCl crystal x-rayed at 80°K (40 min at 50 kvp, 8 ma from a Fe target).

down to half a millimeter or less. Some measurements were taken with load resistors of only 10^8 ohms which further reduced the uncertainty in the wavelength of the maximum. For the weaker bands, however, this could not be done and the slits had to be kept open to 2 mm.

The synthetic crystals were supplied by Harshaw Chemical Company. Natural crystals were chipped out from rocksalt hills near the South-West coast of the Dead Sea (Sodom mountain). These were clear uncolored single crystals. Small slices of about 6×7×1 mm were cleaved out from larger blocks (5–10 cm in dimensions), and used for the measurements. Cleavage surfaces of the natural crystals were less perfect than those of the synthetic ones.

RESULTS

(a) General Features of the Glow Curves

Glow curves were obtained for a large number of synthetic and natural NaCl crystals. They were found to exhibit a complexity of peaks in the temperature range examined (80–600°K). Relative intensities of the various peaks depend on many factors; e.g., the thermal history of the crystal, the x-ray dosage to which it has been subjected prior to the measurements, and the temperature of x-irradiation. It is well known[1,6] that peaks at higher temperatures appear very weak on short x-irradiation at low temperatures. Measurements of peaks above room temperatures were, therefore, taken separately after irradiating the crystals at room temperature.

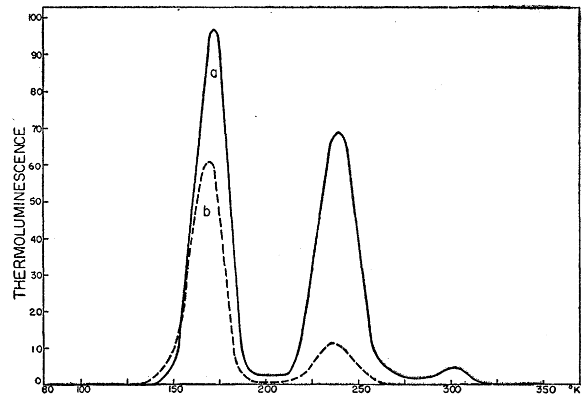

FIG. 3. Glow curves for a synthetic crystal (*a*), and a natural one (*b*), x-rayed (15 min at 35 kvp 14 ma from a Cu target) at 80°K. Both the crystals were pretreated for about 15 min at 550°C.

Glow curves of virgin crystals, especially those of synthetic ones, were comparatively weak, and differed considerably from one specimen to another. As with KCl crystals, the glow could be enhanced by thermal pretreatment. Figure 2 shows a glow curve of a synthetic crystal which has been "aged" by repeated cycles of x-irradiation at low temperature and warming up to about 600°K. The strongest peak appears at 170°K, weaker peaks at 235 and 300°, and still weaker ones at 200, 270, and 125°K. Another very weak peak appears at 100°K only in virgin crystals. Figure 3 shows two more examples of glow curves taken at liquid-air temperature, one for a synthetic crystal (curve *a*), and one for a natural crystal (curve *b*). Although there are differences in the relative intensities of the various peaks in both the glow curves, they do not seem to differ more than is often obtained for two synthetic specimens treated in a similar way.

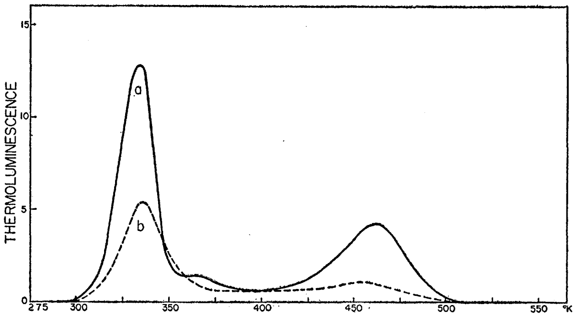

FIG. 4. The same as Fig. 3, but with the crystals x-rayed 1 hour at room temperature.

Figure 4 shows the glow curves for temperatures above room-temperature of the two crystals used for Fig. 3 but x-rayed at room temperature. The main peaks above room-temperature appear at 335 and 475°K. A fuller list of the peak temperatures for NaCl is given in Table I. It should, however, be noted that the peak temperatures change with the rate of warming up of the crystal,[3] and with the dose of x-rays.[7] In addition, it is shown below that most of the glow peaks which appear as well separated single peaks (e.g., the peak at 170°K), are in fact composed of more than one component. Changes in the relative intensities of the components within such a composite peak should, of

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[6] J. J. Hill and P. Schwed, J. Chem. Phys. **23**, 652 (1955).

[7] To be discussed elsewhere; see also reference 4.

TABLE I. Peak temperatures (T_g), relative intensities (I_r) and wavelengths (λ) of the various peaks in the glow curve of NaCl crystals. v.w.—very weak, w—weak, m—medium, s—strong, v.s.—very strong. Intensities are given for thermally untreated, or for slightly treated crystals.

T_g (°K)	100	120	155	170	200	235	270	295	335	375	400	470	520	560
I_r	v.w.[a]	v.w.	m[b]	v.s.	w	v.s.	v.w.	m	s	w	v.w.	m	w[c]	v.w.
λ (μ)	?	?	0.41 0.435	0.365[d]	0.354	0.354 0.37	0.37 ?	0.37	0.365[d] (0.435)	0.51	?	0.47 0.50	0.365[d]	?

[a] Enhanced by heat treatment in a Na atmosphere.
[b] Very strongly enhanced on prolonged heat treatment.
[c] Strongly enhanced on prolonged x-irradiation.
[d] The value 0.365 is probably obtained by superposition of the two components: 0.354 and 0.37 μ.

course, result in an apparent shift in the maximum. Such effects do occur on changing the amount of x-irradiation, the temperature of irradiation, as well as after thermal pretreatment of the crystal. In spite of all these effects peak temperatures may be considered typical, and at constant warm up rates (15° per min in the present work) they remained nearly constant.

(b) Effects of Thermal Pretreatment

These effects are similar to those obtained with KCl crystals.[2] In these experiments, a given crystal was submitted to repeated cycles of heat treatment in the open air at 550°C, cooling to the temperature at which it had been given a constant x-ray dosage, when finally the glow curve was recorded. Figure 5 shows the effect of the accumulated heating time on the thermoluminescence below room-temperature. The same is given in Fig. 6 for the peaks above room temperature. The curves for the virgin crystal are given on an increased scale [50× in Fig. 5(a), and 10× in Fig. 6(a)]. The growth in the thermoluminescence caused by the heat treatment was by a factor of the order of 10^3, and in some cases it was as high as 3000.

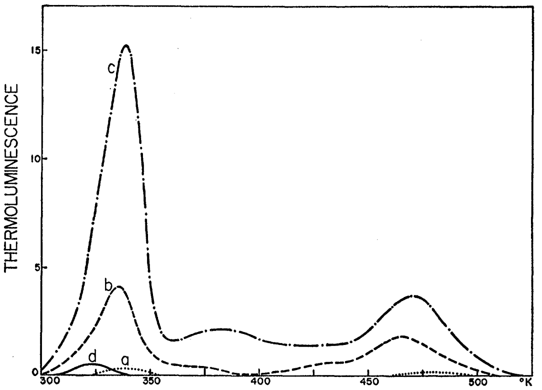

FIG. 6. As Fig. 5 but each curve after 1 hour of x-raying at room-temperature. Pretreatment times: a—virgin, b—5 min, c—135 min, and d—44 hours (at 550°C). The scale for curve a is given ×10.

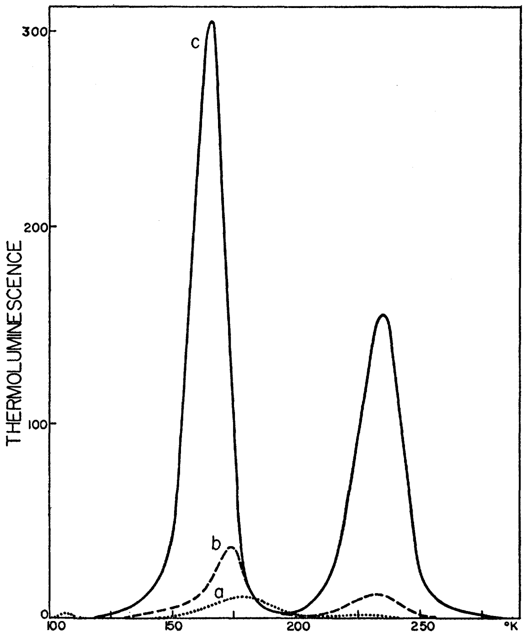

FIG. 5. Effect of heat-treatment on thermoluminescence. Each curve after 15 min of x-irradiation at 80°K (35 kvp, 14 ma, Cu target). Curve a—virgin crystal (scale ×50); b—after 5 min and c after 44 hours of pretreatment at 550°C.

The heat-treatment does not change the temperature of the maximum. The peak at 170°K, however, seems to move to lower temperatures on increasing the heating time. This shift was found to be caused by a satellite at 155°K, which overrides the peak at 170°K, being more sensitive to the heat treatment.

Another point of interest is the different behavior of the various peaks on prolonged heating periods. This is clearly shown in Fig. 7, where the growth of the main glow peaks is plotted on a logarithmic scale against heating time. An extended time scale is given for the short heating periods (up to 45 min), to show the initial growth more clearly. At longer heating times the peaks at 170 and 235°K continue to grow, though tending to saturate, while the peaks at higher temperatures undergo a drop in intensity, which is stronger the higher the peak temperature.

The behavior of different crystals is shown in Fig. 8. Curves a and b were obtained with Harshaw crystals, and curve c with a Dead Sea crystal. The similarity in behavior is remarkable.

One of these crystals was subjected to 120 hours x-

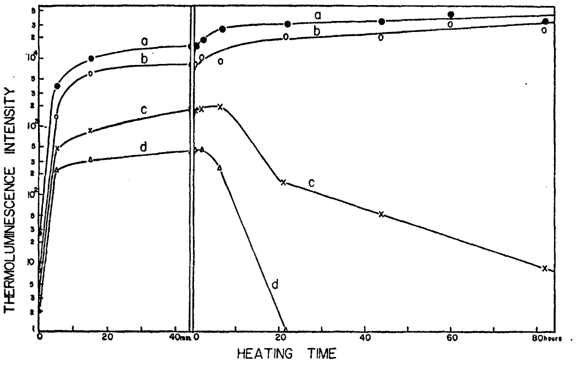

FIG. 7. Effect of heating time on various peaks in the glow curve of NaCl. Curve *a*—the peak at 170°K, *b*—235°K, *c*—335°K, and *d*—470°K. Each point in curves *a* and *b* was obtained after 15 min of x-irradiation at 80°K. In curves *c* and *d*—1 hour at room-temperature (35 kvp, 14 ma, Cu target).

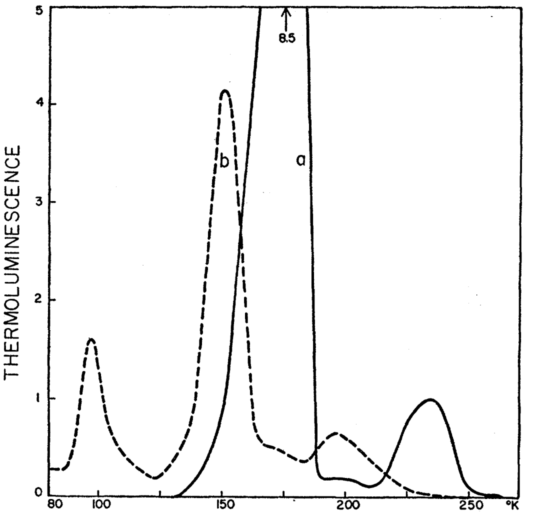

FIG. 9. Effect of pretreatment in a sodium atmosphere on the glow curve of NaCl. Curve *a*—the crystal after 45 min at 550°C; *b*—after additional 3.5 hours in sodium vapor at 550°C.

irradiation (held close to the beryllium window of an x-ray tube with a Cu target, operated at 50 kv, 14 ma). Prior to the irradiation the crystal had been held for a total of 7.5 hours at 550°C. The x-irradiation caused a reduction by a factor of 2 in the thermoluminescence (see the corresponding point on curve *b* Fig. 8). This result fits qualitatively those reported by Spicer,[8] who investigated similar effects on the x-ray luminescence of NaCl crystals. It is of interest that an additional period of heat-treatment brings the sample to a point on the curve (Fig. 8, *b*) which is just a continuation of the part of the curve obtained prior to the prolonged x-irradiation.

In the experiments described above the crystals were heated in the open air. Heating in an atmosphere of sodium vapor resulted in an effect similar to that obtained with KCl crystals.[2] An example is shown in Fig. 9, where curve *a* was obtained with a crystal preheated 45 min at 550°C, and curve *b* for the same crystal after additional heating for 3½ hours in an atmosphere of sodium vapor at 550°C. The latter treatment caused the peaks above room temperature (not shown in the figure) to disappear, and the same happened with the peaks at 170 and 235°K. On the other hand, the peak at 100°K appears fairly strong and that at about 150 is now the strongest. The same effect was obtained both with natural and synthetic crystals.

(c) Thermoluminescence Spectra

The spectra of the light emitted at the various glow peaks of NaCl crystals appear to be more complex than that of KCl. Close examination, however, reveals some regularities. An important point in the results is that peaks with the same wavelength are repeated several times throughout the temperature range between 80 and 600°K.

In the following figures, spectra are given as photocopies of the traces on the oscilloscope screen. The wavelength calibration for these spectra is given in Fig. 10.

Figure 11 shows a collection of spectra taken just at the peak-temperatures of the main glow peaks. Photographs *a*–*d* were obtained with a synthetic crystal. The

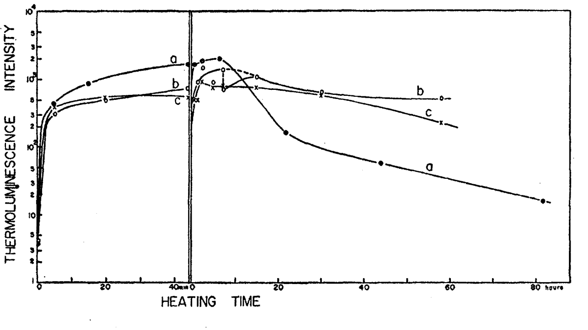

FIG. 8. Effect of heating time on different crystals. Curves *a* and *b* for synthetical crystals; *c*—for a natural one; all at 335°K.

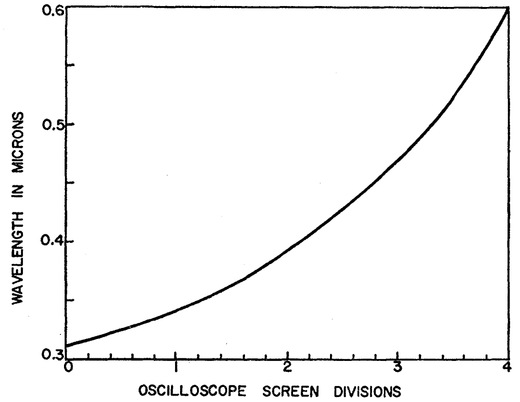

FIG. 10. Wavelength calibration for the spectra on the oscilloscope screen.

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[8] W. E. Spicer, Phys. Rev. **106**, 726 (1957).

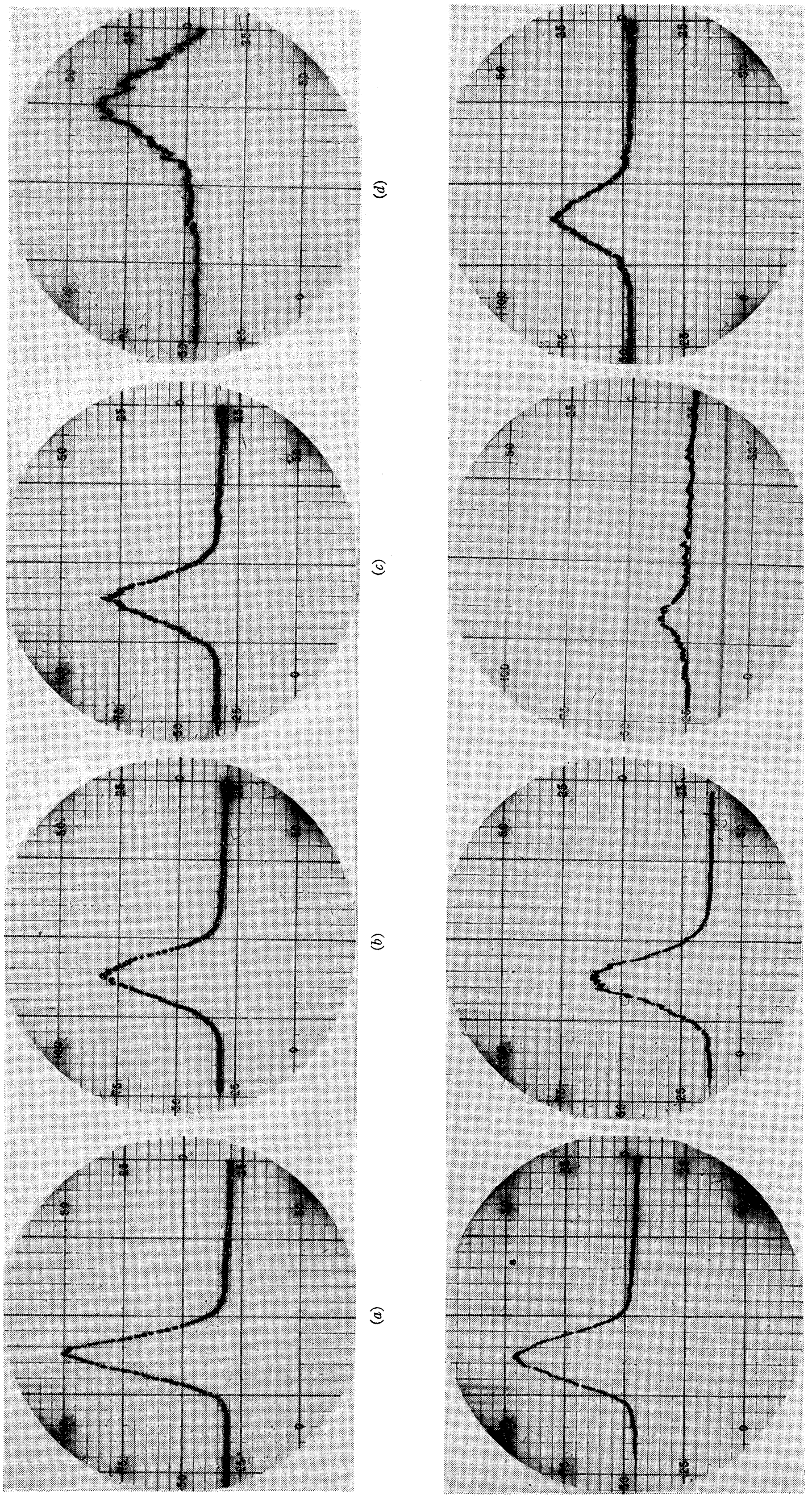


FIG. 11. Spectra taken at various temperatures during the glow. Curves *a*, *b*, *c* and *d*, for a synthetical crystal, taken at 175, 240, 325, and 465°K, respectively. Curves *e* and *f* (natural crystal) taken at 175 and 237°K, respectively. Curves *g* and *h*—at 205, and 290°K, respectively, for synthetical crystals. Amplifier attenuation and monochromator slit-widths differ from curve to curve.

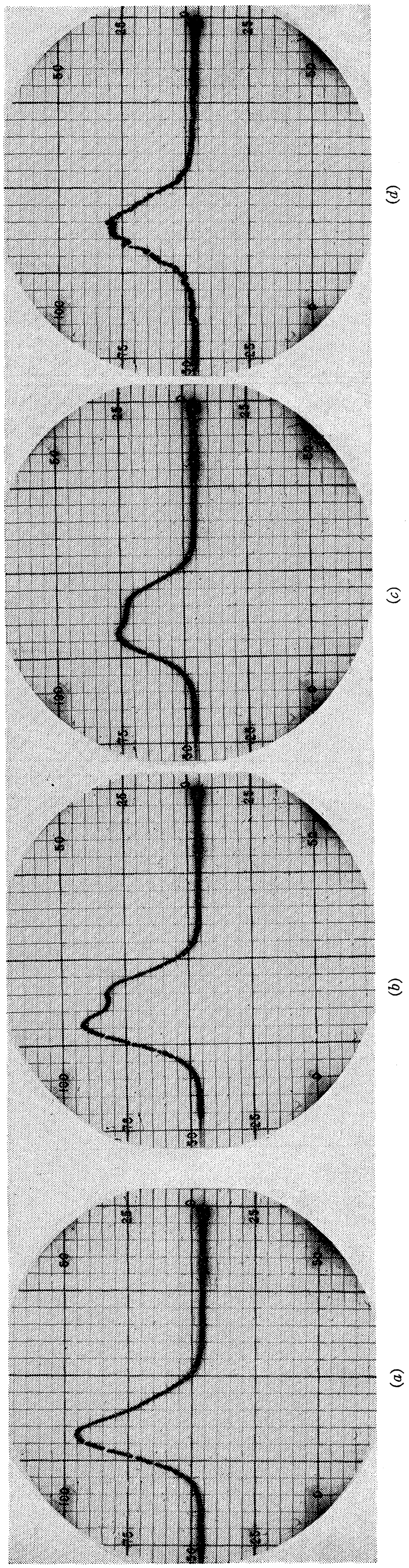


FIG. 12. Transition from the 0.354 μ band to the 0.37 band in the temperature range 220–265°K. Curve *a*—220°, *b*—233°, *c*—238°, and *d*—at 265°K. (Synthetical crystal, heat-treated 75 min at 550°C.) Monochromator slit-width—2 mm.

band at 0.365 μ is repeated at 170, 235, and 335°K [Figs. 11(*a*), (*b*), and (*c*), respectively], while the spectrum of the glow peak at 470°K [Fig. 11(*d*)] is quite different. The wavelength of the maximum of the band is in this case 0.47 μ, and is occasionally resolvable into two components, one near 0.47 and the other at about 0.50 μ. It should be noted that after very long x-irradiations the band at 0.365 μ appears as the dominating one in the temperature region of 500°K.

Figures 11(*e*) and (*f*) are for the glow peaks at 175 and 237°, respectively, this time for a natural crystal. The spectra are just the same as obtained for the synthetic crystal. Spectra for two weaker peaks are shown in Figs. 11(*g*), and 11(*h*) for the peaks at 200 and 295°K, respectively. The former has its maximum at 0.354 μ, and the latter at 0.37 μ.

The small difference in wavelength is not incidental, and in fact the band at 0.36 μ is composed of two independent components. This is shown in Fig. 12, where a series of spectra taken in the temperature range 200–265°K is given. In photograph 12(*a*), at 220°K, the band peaks at 0.354 μ, and a shoulder can be noticed toward longer wavelengths. In 12(*b*), at 233°K, the component at 0.37 μ is already strong. It is comparatively stronger in 12(*c*) (at 238°K), while at 265°K [12(*d*)] it is the dominating one. That the peak at 235°K is composed of more than one component has been verified independently by thermal bleaching experiments, when by partial bleaching, two peaks, at 220 and 240°K, could be obtained partly separated.

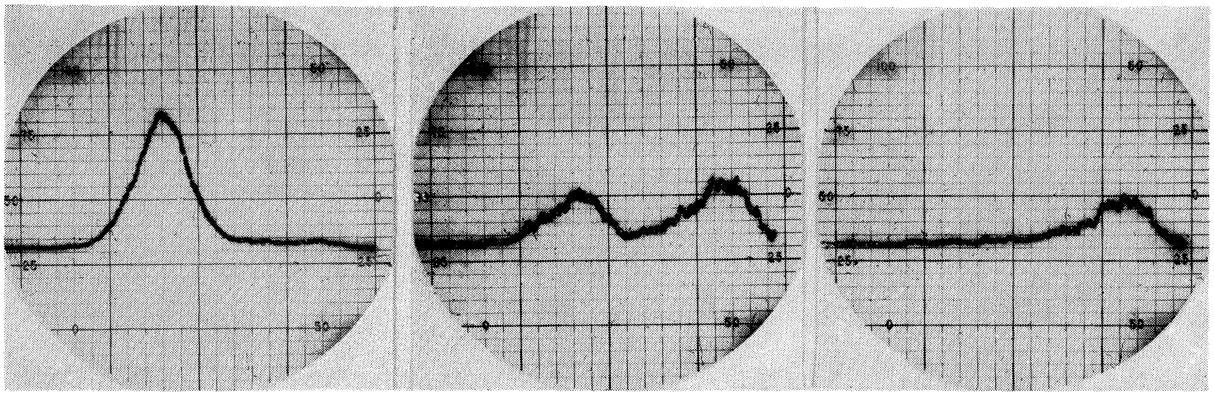
The same pair of bands has been observed for the peak at 170°K (0.37 μ) which passes into the 0.354 μ band near 200°K. There is some evidence for the appearance of the same pair also at higher temperatures (e.g., at 500–520°K), where the two components could not be clearly separated, probably because of temperature broadening.

Another transition from one spectral band to another is shown in Fig. 13. The temperature range is now 330–370°K. At 330°K [Fig. 13(*a*)] the band maximum is at 0.37 μ. A green band (at 0.51 μ) can be seen in 13(*b*) (at 355°), and at 372°K [13(*c*)] only the latter remained.

In addition to the spectral bands mentioned already, bands also appear with maxima at about 0.41 and 0.435 μ. These were, however, weak compared to the 0.365 μ band in virgin or only slightly heat-treated crystals. An example is shown in Fig. 14(*a*) (taken at 345°K), where bands at 0.435 and 0.51 μ appear as weak satellites to the strong 0.365 μ band.

Heat treatment, in addition to enhancing thermoluminescence, also changes the relative intensities of the various components within a given peak. In general, bands of longer wavelengths tend to replace the 0.365 μ one, which is the dominant band in virgin crystals.

The glow at 170°K is replaced by a peak at 155°K (see paragraph *b* above). The corresponding change in the spectrum is shown in Figs. 14(*b*), (*c*), and (*d*). Figure 14(*b*) was obtained with the crystal after a short



(*a*) (*b*) (*c*)

FIG. 13. Transition from the 0.37 μ band to the 0.51 band in the 330–370°K range. *a*—at 330°, *b*—355°, and *c*—at 372°K. Synthetical crystal, after 15 min at 550°C. X-rayed for 1 hour (35 kvp, 14 ma, Cu target).

period of heat treatment at 550°C. Here the 0.435 μ band is still weak. The 0.41–0.435 μ bands are already as intense as the 0.365 μ band in Fig. 14(*c*), obtained after 22 hours at 550°C, while in Fig. 14(*d*) (66 hours at 550°C), the maximum appears at 0.41 μ with only extended shoulders towards shorter and longer wavelengths.

The peak at 235°K behaves differently, and its spectral distribution (0.365 μ) remains practically unchanged even after 66 hours of the crystal at 550°C.

The results are summarized in Table I, where the peak-temperatures for the glow of NaCl crystals are given together with the wavelengths of the spectral bands and indications of the relative intensities of the various peaks.

An attempt was also made to measure the spectral band widths. This, however, was found difficult because of the interference of neighboring bands. The width of the 0.37 μ band at 235°K was found in these measurements to be about 0.25 ev.

DISCUSSION

The thermoluminescence of NaCl has been studied by many investigators.[4,6,9–11] Some of them attempted also to measure the spectral distribution of the emitted light.

Adler and Stegmüller[9] photographed the glow by warming up many NaCl crystals in succession in front of the slit of the spectrograph. They found that the main band had its maximum at 0.36 μ. Hill and Schwed,[6] using a conventional spectrophotometer observed four bands: at 0.362, 0.418, 0.432 μ, and a very weak one at 0.525 μ. No more details could be given by these authors because of the small intensity and the transient nature of the emitted light. These authors restricted their measurements to temperatures above room temperature. In addition they did not measure individual peaks in the glow. More recently Dutta and Ghosh[11] examined the thermoluminescence spectra of some alkali-halides including NaCl. They used a rapid-scanning spectrophotometer, but with the photomultiplier at room temperature. To get a good signal to noise ratio, they had to use high warming rates (6–7 deg per sec). They also used powder samples instead of single crystals, and 10-kv cathode rays for irradiation instead of 35-kv x-rays in our experiments. Three peaks in the glow curve of NaCl were detected by Dutta and Ghosh, one at 160°K with band maxima at 0.432, and 0.54 μ, one at 232°K (0.484 μ), and a third one at 545°K (0.416, 0.519 μ). The spectra do not fit at all our results; e.g., the 0.365 μ band, which is the dominant one in our experiments, does not appear at all in the results given by Dutta and Ghosh. The disagreement should be attributed partly to differences between powders and single-crystals, and partly to the experimental differences described above.

The results reported by Hill and Schwed[6] are in better agreement with ours. The 0.362 μ band reported by these authors fits well the mean of the pair 0.354, 0.37 μ obtained by us. The same applies to the pair 0.418, 0.432 μ which fits ours at 0.41, 0.435 μ. At longer wavelengths we observed bands with maxima at 0.47 and 0.50–0.51 μ. The latter seems to correspond to the green band at 0.525 μ reported by Hill and Schwed. It should be noted that we did not correct for the variation with wavelength of the sensitivity of the photomultiplier (RCA *IP*28), which might explain the small discrepancy between the wavelength given by us and that found by Hill and Schwed.

It is also of interest to compare our results to those obtained for the luminescence of NaCl crystals excited by uv light or by x-rays. Maenhout-van der Vorst[12] found that "pure" NaCl crystals, excited by uv light (0.26 μ), emitted two luminescence bands at 0.356 and 0.424 μ, while another band at 0.55 μ was observed with oxygen contaminated samples.

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[9] H. Adler and F. Stegmüller, Acta Phys. Austriaca **11**, 31 (1957).

[10] L. F. Heckelsberg and F. Daniels, J. Phys. Chem. **61**, 414 (1957).

[11] B. C. Dutta and A. K. Ghosh, Indian J. Phys. **32**, 578 (1958).

[12] W. Maenhout-van der Vorst, Physica **24**, 996 (1958).

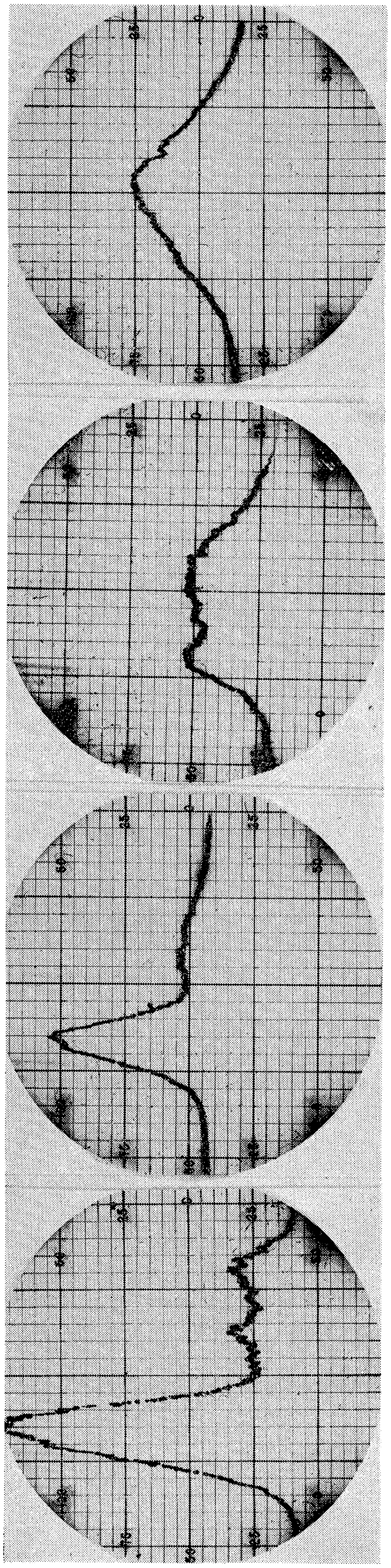

Fig. 14. Curve *a* taken at 345°K, after 15 min at 550°C, *b*, *c*, and *d* taken at about 170°K, but preheated at 550°C for 5 min, 22 hours, and 62 hours, respectively.

Spicer[8] observed in x-ray luminescence of NaCl almost all the spectral bands which appear in our experiments. Only one band at 5 ev ($0.248\ \mu$), the strongest in the x-ray luminescence, does not appear in our thermoluminescence spectra.

Heat pretreatment seems to affect the uv excited luminescence, the x-ray luminescence, and the thermoluminescence in a similar way. There is, however, a quantitative difference. While the x-ray luminescence is enhanced by a factor of about 20 by heat treatment,[8] the enhancement in the thermoluminescence found in the present work was enhanced by a factor of the order of 1000. The explanation might be that in the case of x-ray luminescence we have enough electrons ready for recombination, and the enhancement is caused only by the increase in the luminescence yield of the recombination process. In the thermoluminescence process, on the other hand, there might also be an increase in the efficiency in supply of carriers for radiative transitions.

The effects of heat pretreatment observed in the present work are similar to those obtained previously with KCl crystals.[2] Just as in the previous work, we assume that in addition to the diffusion of oxygen into the crystal, there is also another process of diffusion, namely the migration of positive-ion vacancies and holes from the outer surfaces of the crystal into the interior. At the same time internal diffusion of vacancies inside the bulk of the crystal causes them to become more evenly distributed. This might explain why at very long heating times glow peaks at higher temperatures disappear, while other peaks at lower temperatures still continue to grow. Assuming that glow peaks at higher temperatures involve migration of the carriers to non-neighboring recombination centers, these should be reduced in intensity if the positive ion vacancies and the negative ion vacancies approach each-other after prolonged heat treatment.

The fact that peaks emitting just the same wavelengths are repeated in the glow curves of NaCl is in contradiction to the model proposed by Bonfiglioli *et al.*,[4] according to which the light of each thermal peak must have its own wavelength. Another implication of this model, namely that the activation energy E should be the same for all the peaks in the glow curve, has not been confirmed in our laboratory.[13]

We assume that at a given glow peak carriers of a given sign (for some peaks they may be electrons and for others, holes) are released thermally and may emit light on recombination. The efficiency of radiative recombination is, however, usually very small,[14] probably due to the lack of intermediate steps which seem to be necessary for the recombination process. The role of the oxygen might be to supply these intermediate steps. Evidence that the transitions are not direct also appears

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[13] A. Halperin *et al.* (to be published).

[14] See, for example, D. Dutton and R. Maurer, Phys. Rev. **90**, 126 (1953).

from the energies of the emitted light which are about 2.5–3.5 ev, while direct recombination of a free hole, for example, with an electron in an F center should result in the emission of about 6 ev.

Finally, mention should be made of the appearance in pairs of the spectral bands in the thermoluminescence. The three pairs: 0.354–0.37, 0.41–0.435, and 0.47–0.50 μ observed in the present work seem to have a common energy difference of about 0.16 ev within each pairs. More accurate determination of these separations is necessary before the existence of such a doublet is confirmed. It is of interest to note that a doublet of about 0.15-ev separation has been observed[15] in the exciton-band of NaCl.

The investigation is now extended in our laboratory to include other alkali-halides with the hope that it will lead to better understanding of the effects described.

[15] P. L. Hartman, Phys. Rev. **105**, 123 (1957).

PHYSICAL REVIEW VOLUME 116, NUMBER 5 DECEMBER 1, 1959

Antiferromagnetic Linear Chain

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(Received June 4, 1959)

Orbach's integral equation which leads to the value of the ground-state energy of an anisotropic antiferromagnetic linear chain of spins, $S=\frac{1}{2}$, has been solved. The result is then expanded in powers of the anisotropy parameter. In this form it corresponds to the result of a perturbation calculation, the transverse part of the Hamiltonian being the perturbation. The rapid convergence of the energy series even for the isotropic case and the adequate convergence of that for the short range order, suggests that the result given by perturbation theory for the sublattice magnetization may also be satisfactory.

ORBACH[1] has recently considered the antiferromagnetic linear chain with an Ising type of anisotropy. The Hamiltonian of the system is taken to be, for a chain of N spins with $S=\frac{1}{2}$,

$$H=2J\sum_i \left(S_i^zS_{i+1}^z+\beta(S_i^xS_{i+1}^x+S_i^yS_{i+1}^y)\right)$$
$$=2J\sum_i \left(S_i^zS_{i+1}^z+(\beta/2)(S_i^+S_{i+1}^-+S_i^-S_{i+1}^+)\right),$$
$$1\leqq i\leqq N.$$

If E is the ground-state energy and a quantity ϵ is defined by

$$\epsilon=-(1/2J)(E-\tfrac{1}{2}JN), \tag{1}$$

Orbach shows that

$$\epsilon=\frac{N}{2}\int_0^{2\pi}(1-\beta\cos k)A(k)dk, \tag{2}$$

where $A(k)$ is a solution of the integral equation

$$A(k)=\frac{1}{\pi}-\frac{1}{2\pi}\int_0^{2\pi}dk'\times\frac{(1-\beta\cos k')A(k')}{1-\beta(\cos k+\cos k')+\beta^2\cos[(k+k')/2]}. \tag{3}$$

This equation he solved numerically. By a suitable change of variables (3) may be solved by a Fourier expansion.

We define λ by the relation $\beta=\operatorname{sech}\lambda$, with $\lambda>0$, introduce an angle ψ related to k by the equation

$$e^{i\psi}=\frac{e^\lambda-e^{ik}}{1-e^{\lambda+ik}},$$

and replace $A(k)$ by $B(\psi)$, where

$$B(\psi)(e^{i\psi}-e^\lambda)(e^{i\psi}-e^{-\lambda})=A(k).$$

The integral equation (3) becomes

$$B(\psi)=[\pi(e^{i\psi}-e^\lambda)(e^{i\psi}-e^{-\lambda})]^{-1}-\frac{e^{2\lambda}-e^{-2\lambda}}{\pi}\int_0^{2\pi}\frac{e^{2i\psi}B(\psi')d\psi'}{(e^{-\lambda+i\psi'}-e^{\lambda+i\psi})(e^{-\lambda+i\psi}-e^{\lambda+i\psi'})},$$

and has a solution in the form of a series of powers of $e^{i\psi}$. The expression for $B(\psi)$ is

$$B(\psi)=-\frac{1}{\pi}\frac{2}{e^\lambda-e^{-\lambda}}\sum_{-\infty}^{+\infty}\frac{e^{im\psi}}{\cosh|m+1|\psi},$$

or

$$A(\psi)=-\frac{1}{2\pi}\frac{\cos\psi-\cosh\lambda}{\sinh\lambda}\sum_{-\infty}^{+\infty}\frac{e^{im\psi}}{\cosh m\psi}.$$

When this form is introduced into (2) the ground-state energy is found to be given by

$$E=NJ\left[\tfrac{1}{2}-\tanh\lambda\left(1+\sum_1^\infty\frac{4}{e^{2n\lambda}+1}\right)\right]. \tag{4}$$

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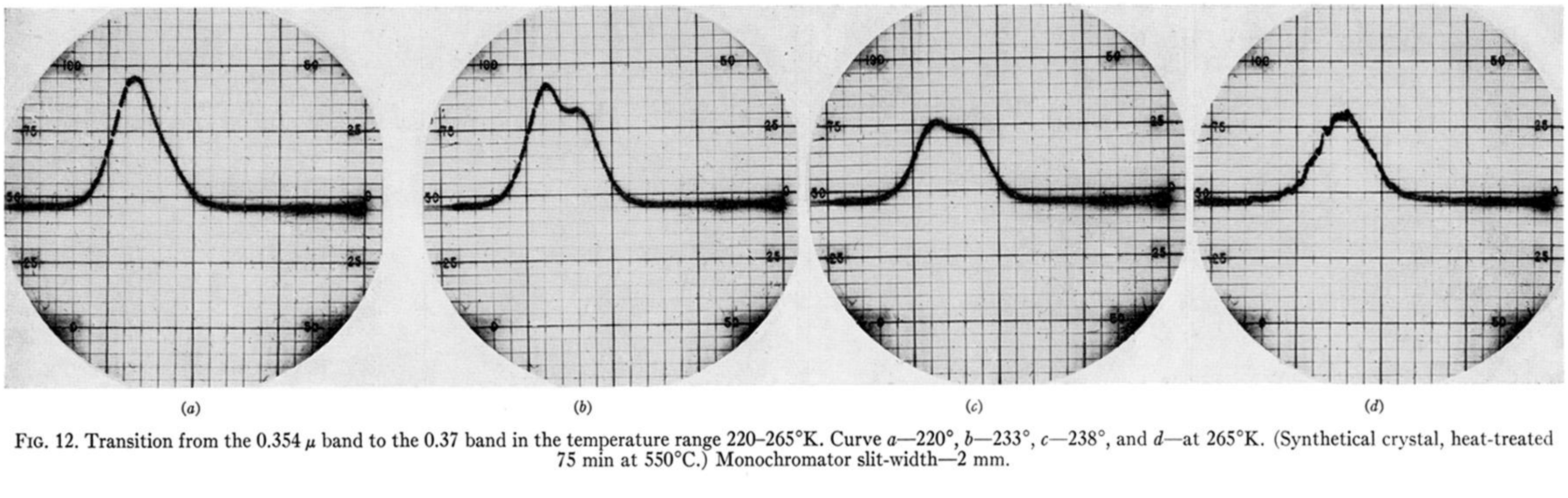
[1] R. Orbach, Phys. Rev. **112**, 309 (1958).

(a) (b) (c) (d)

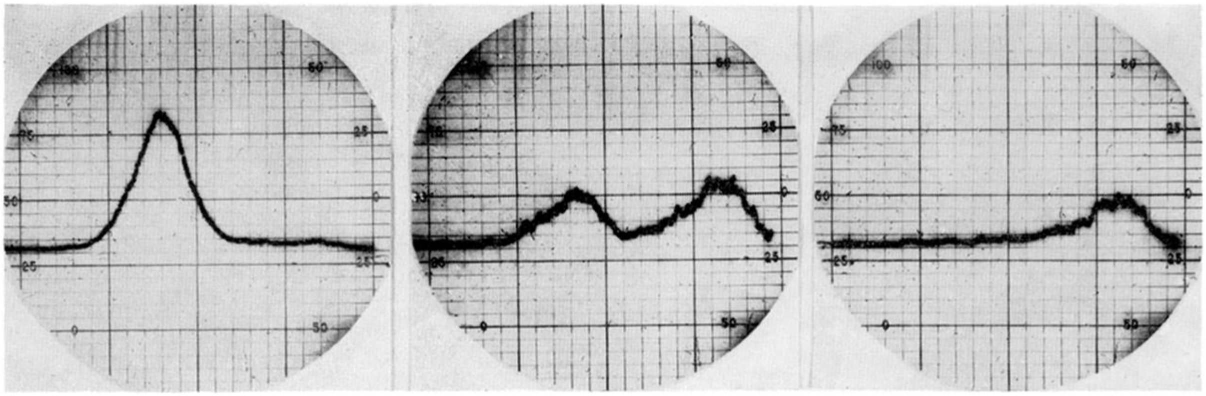
(e) (f) (g) (h)

FIG. 11. Spectra taken at various temperatures during the glow. Curves *a*, *b*, *c* and *d*, for a synthetical crystal, taken at 175, 240, 325, and 465°K, respectively. Curves *e* and *f* (natural crystal) taken at 175 and 237°K, respectively. Curves *g* and *h*—at 205, and 290°K, respectively, for synthetical crystals. Amplifier attenuation and monochromator slit-widths differ from curve to curve.



(a) (b) (c) (d)

FIG. 12. Transition from the 0.354 μ band to the 0.37 band in the temperature range 220–265°K. Curve *a*—220°, *b*—233°, *c*—238°, and *d*—at 265°K. (Synthetical crystal, heat-treated 75 min at 550°C.) Monochromator slit-width—2 mm.



(*a*) (*b*) (*c*)

FIG. 13. Transition from the 0.37 μ band to the 0.51 band in the 330–370°K range. *a*—at 330°, *b*—355°, and *c*—at 372°K. Synthetical crystal, after 15 min at 550°C. X-rayed for 1 hour (35 kvp, 14 ma, Cu target).

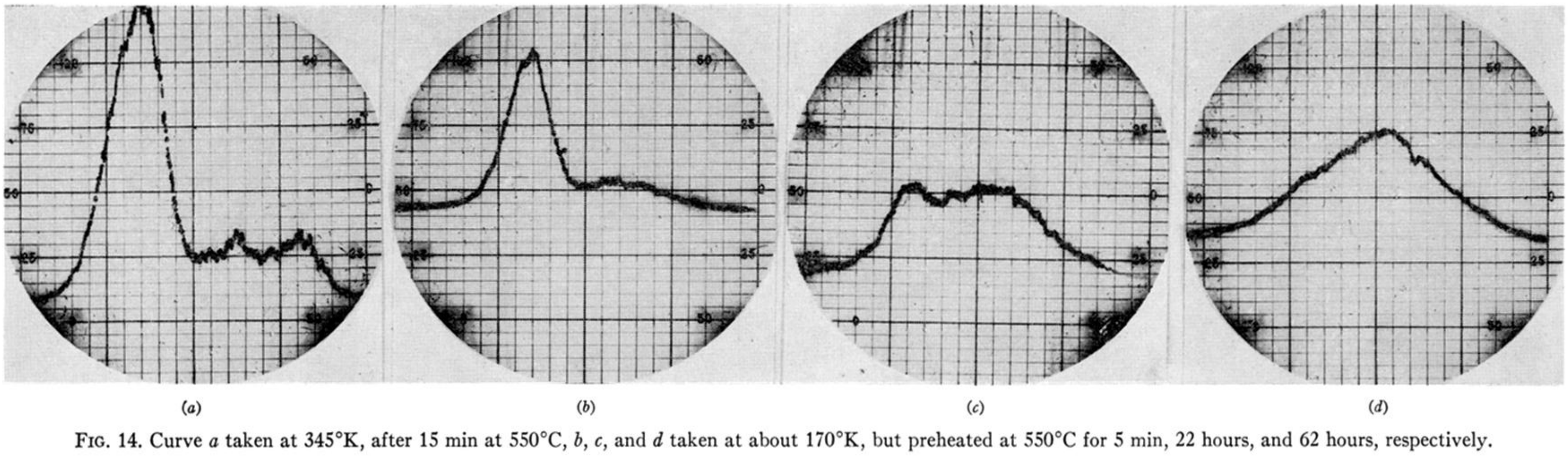

(a) (b) (c) (d)

FIG. 14. Curve *a* taken at 345°K, after 15 min at 550°C, *b*, *c*, and *d* taken at about 170°K, but preheated at 550°C for 5 min, 22 hours, and 62 hours, respectively.