it is assumed that the spin system is at any time in thermal equilibrium with a spin temperature, different from that of the molecular surroundings; a measure for the relaxation time is then obtained from the rate of energy transfer to the molecular surroundings. As mentioned in the Introduction of this paper, the generalization of the method of Wangsness and the author, presented in II, would likewise permit such a treatment of this problem, but it could be applied only for a sufficiently high intensity of the fixed magnetic field. Redfield's results, however, can also be applied to relaxation in an arbitrary small field which is of considerable experimental interest. The author is grateful to Dr. Redfield for having received his manuscript before publication and for an interesting discussion.

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Luminescence of Potassium Iodide*

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When single crystals of potassium iodide are cooled to $-160°$C and illuminated with light absorbed in the first fundamental band they luminesce with a quantum yield between 0.5 and 1. The excitation and emission spectra of this luminescence are presented. The experiments suggest that pure KI itself luminesces under the above conditions and that the luminescence can be modified by the presence of impurities or defects in the lattice.

I. INTRODUCTION

BECAUSE of their simple structure the alkali halides have played a very important role in the development of solid-state physics and it appears that there is still much to be learned from experiments done on them. For example, consider the result of illuminating a crystal with light absorbed in the first fundamental band. According to one interpretation this results in the excitation of electrons on the negative ions in the lattice. One observes, however, that this also results in a change in the optical properties of the crystal. *F* centers, among other things, appear in the lattice during illumination.[1] It is also found that *F* centers may be ionized by illumination with fundamental band light.[2] This type of observation suggests that the energy of an excited negative ion is not localized at the absorption site but may be transferred through the lattice and produce effects some distance from the point of absorption. Theoretically it is also found that such energy transfer is possible and several mechanisms for the transfer have been proposed.[3] However, it has not as yet been experimentally determined which of these mechanisms is important in the alkali halides.

Another way in which the excited negative ion can get rid of its energy is by the emission of a quantum of light. There is apparently no theoretical reason why this process cannot occur in the alkali halides, but until quite recently no experimental observations of luminescence of these substances during illumination in the fundamental band have been taken seriously. Because of this, it has been generally accepted that such luminescence does not occur. In the past few years, however, several workers have reported a low-temperature luminescence which might be ascribed to pure alkali halides, while others have observed fundamental band luminescence which was apparently connected with the presence of defects in the lattice.[4] The present work was motivated in part by the work mentioned above and also by the realization that a study of the luminescence of single alkali halide crystals excited by illumination in the fundamental band can perhaps help solve the problem of energy transfer mentioned in the first paragraph. It is interesting to determine whether or not the pure, perfect alkali halides will luminesce, but perhaps more important is the use of emission initiated by the excitation of a negative ion in the lattice as a tool in the investigation of energy transfer phenomena. Some experiments to this effect are discussed in the conclusion of this paper.

II. EXPERIMENTAL

In this paper the luminescence of the potassium iodide will be described in terms of its excitation and emission spectra and the quantum yield. Also, the optical absorp-

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[1] A. Smakula, Z. Physik **63**, 762 (1930).

[2] E. Taft and L. Apker, Phys. Rev. **81**, 698 (1951); **82**, 814 (1951); **83**, 479 (1951). N. Inchauspé and R. J. Maurer, Air Force Technical Note OSR-TN-55-281 (unpublished).

[3] D. L. Dexter and W. R. Heller, Phys. Rev. **84**, 377 (1951); W. R. Heller and A. Marcus, Phys. Rev. **84**, 809 (1951); D. L. Dexter and J. H. Schulman, J. Chem. Phys. **22**, 1063 (1954).

[4] W. van Sciver and R. Hofstadter, Phys. Rev. **97**, 1181 (1956); W. Martienssen, Z. Physik **131**, 488 (1952); W. Martienssen and R. W. Pohl, Z. Physik **133**, 153 (1952); W. Martienssen, Nachr. Akad. Wiss. Göttingen Kl. IIa, No. 11, 111 (1952).

tion of the crystals used is important. These quantities and the methods used to measure them are discussed in the following paragraphs.

1. Excitation Spectra

The excitation spectra shown below were measured in the following way. The crystals were exposed, in a cryostat, to light from a quartz monochromator. The luminescence of the crystal as a function of the photon energy of the incident light was measured with a photomultiplier whose optical axis was set perpendicular to the beam from the monochromator. The quantity called "total luminescence" on the excitation spectra graphs is proportional to the current in this photomultiplier. Since most of the quanta emitted by the crystal had energies in a region where the response of the photomultiplier was quite flat, the quantity "total luminescence" is approximately proportional to the total number of photons emitted for a given energy of excitation light.

In measuring the excitation spectra the number of exciting quanta was held constant. To do this it was necessary to vary the band pass of the monochromator. At 2140 A the band pass was 5 A. At longer wavelengths it was no greater than this.

2. Emission Spectra

To make emission spectra measurements two quartz monochromators were used; one to provide exciting radiation, the other to analyze the light emitted from the crystals. The output of the second monochromator was measured with a photomultiplier held at its exit slit. The current in this photomultiplier, after correction for the spectral dependence of the photomultiplier response, was thus proportional to the total number of quanta emitted by the potassium iodide crystal in an energy interval equal to the band pass of the monochromator, assuming the monochromator transmission to be flat. This quantity was converted into "relative number of photons per unit band pass" by dividing by the band pass of the scanning monochromator. In the emission spectra the band pass of the monochromator providing the excitation radiation was 0.02 ev at 5.90 ev and 0.015 ev at 5.65 ev. The total number of quanta incident on the crystal was held constant at 6.25×10^{12} per sec. The band pass of the analyzing monochromator was 0.035 ev at 4.00 ev and 0.065 ev at 2.50 ev.

3. Quantum Yield

The quantum yield of luminescence is defined as the total number of quanta emitted by the crystal over the total number absorbed. It was measured by means of a calibrated end-on photomultiplier held at a known distance from the crystal. The fraction of emitted quanta incident on the photomultiplier was approximated from the ratio of the area of the photomultiplier cathode to the total area of a sphere with radius equal to the distance from cathode to crystal. The crystal was illuminated with a known number of quanta from a quartz monochromator. All quantum yield measurements were made with exciting light of energy 5.75 ev. At this energy the band pass of the monochromator was 0.06 ev with the slit widths used. The quantum yields are corrected for the transmission of the windows of the cryostat. Reflection of the crystal was assumed to be 30% at 5.75 ev in calculating the yields.

4. Optical Absorption

The optical absorption of the three crystals used is presented in terms of optical density which is defined as $D=\log_{10}(I_0/I)$, where I_0 is the incident intensity of measuring light and I is the transmitted intensity. The absorption curves were roughly corrected for reflection losses by subtracting an amount equal to the reflection of the crystal at 4.0 ev, where the absorption should be negligible.

5. Crystals

Two of the crystals used, those numbered 1 and 3, were obtained from the Harshaw Chemical Company. They both contained a small amount of thallium although they were supposed to be pure KI. The optical absorption curve of crystal 1 indicates that it was quite a good crystal. No thallium absorption bands appear. The presence of thallium is indicated only by the excitation spectrum of this crystal. Crystal number 3 contained enough thallium to affect both the optical absorption spectrum and the excitation spectrum. It was also possible to observe the thallium emission bands in the case of this crystal.

Crystal number 2 was obtained from Dr. G. Chiarotti of the University of Illinois, who grew it from reagent grade material. It was crystallized twice. The optical absorption spectrum of this crystal shows no definite impurity bands but indicates that it may have been somewhat strained.

III. DISCUSSION

1. Excitation Spectra

In the following discussion it should be remembered that, since the number of excitation photons was held constant, the quantity "total luminescence" can be taken as closely proportional to the quantum yield in regions of total light absorption if one is willing to neglect reflection losses. The regions of total absorption can be determined from the optical absorption data shown in Figs. 1 to 3.

At room temperature no significant excitation bands appear other than the well-known thallium bands in crystals 1 and 3. These are shown at 4.35 ev and 5.20 ev in the curves marked 2 in Figs. 4 and 6. When the crystals were cooled to −160°C illumination with light

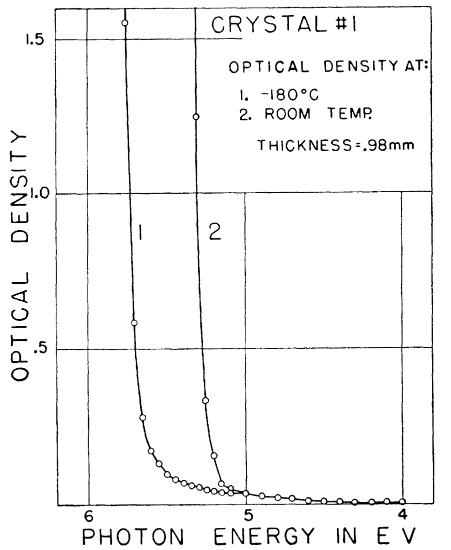

FIG. 1. Optical absorption spectrum of crystal 1. No thallium bands are apparent.

absorbed in the first fundamental band caused a strong luminescence as is shown by the curves marked 1 in Figs. 4, 5, and 6. The quantum yield increased by more than a factor of 10^2 at an excitation energy of 5.75 ev during the cooling. In the case of crystal 3 the thallium excitation bands appear at 5.35 ev and 4.4 ev, shifted slightly from their room temperature positions. These bands also appear with much less intensity in the spectrum of crystal 1 and perhaps in the spectrum of crystal 2. In all cases the thallium bands appear to be superimposed on the tail of a large excitation band or bands occupying the same spectral region as the first fundamental band of potassium iodide. In all three cases the excitation spectrum of the fundamental band luminescence has the same general form and the peaks which occur at 5.75 ev and 6.0 ev are about the same height. The similarity of the excitation spectra, excluding the peaks contributed by the thallium, suggests that the luminescence caused by irradiation in the first fundamental band is a property of pure potassium iodide, since the different histories of the crystals make it improbable that they all contained the same concentration of any impurity.

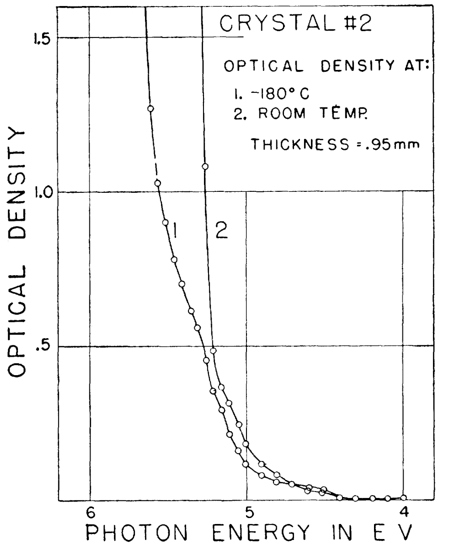

FIG. 2. Optical absorption spectrum of crystal 2.

The deep minimum which occurs at 5.8 ev in the excitation spectra taken at −160°C is very interesting. In the case of crystal 3 (Fig. 6) the minimum indicates a decrease in the quantum yield by a factor of 10. It is to be noted that this minimum occurs quite close to the position of the optical absorption maximum which lies at 5.78 ev in potassium iodide at this temperature, according to Fesefeldt.[5] An increase in reflection loss, which does occur near the absorption maximum, would account for some decrease in quantum yield, but not for a decrease of a factor of 10, certainly. Near the peak of the first fundamental band the light is absorbed within 1000 A of the crystal surface and in this region some surface modification of the bulk lattice structure may cause quenching of the luminescence.

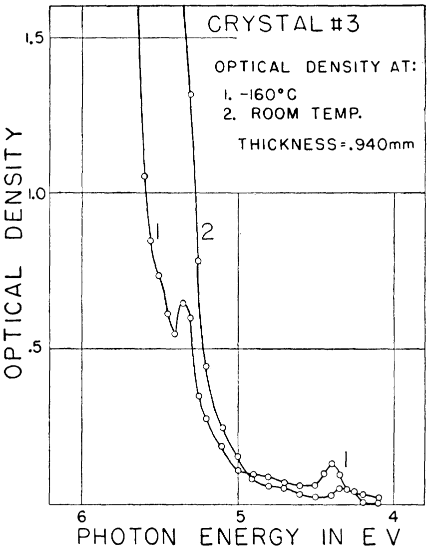

FIG. 3. Optical absorption spectrum of crystal 3. Note the thallium bands on the tail of the fundamental band.

The tail of the first fundamental band of crystal 1, as shown in Fig. 1, was quite sharp. This indicates that crystal 1 was not greatly strained and that no great number of defects were present in the lattice. The fundamental band tail of crystal 2, however, was somewhat distorted as is shown in Fig. 2. For example, crystal 2 absorbed about 4 times as much light as crystal 1 at 5.0 ev and −180°C. The total luminescence of crystal 2 was twice that of crystal 1 at −160°C, as

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[5] H. Fesefeldt, Z. Physik **64**, 741 (1930).

shown by the excitation spectra. One can speculate that in general the properties of the luminescence caused by irradiation in the fundamental band tail region will be dependent on the perfection of the crystal.

2. Emission Spectra

The emission spectra are shown in Figs. 7, 8, and 9 for crystals 1, 2, and 3. First let us discuss the differences between the emission of crystal 1 and crystal 2. Upon excitation with 5.9-ev light a single emission band appeared in the region from 2.0 ev to 5.5 ev as is shown by curve 1, in Figs. 7 and 8. This band has its peak at 3.3 ev and a half-width of about 0.7 ev in both cases.

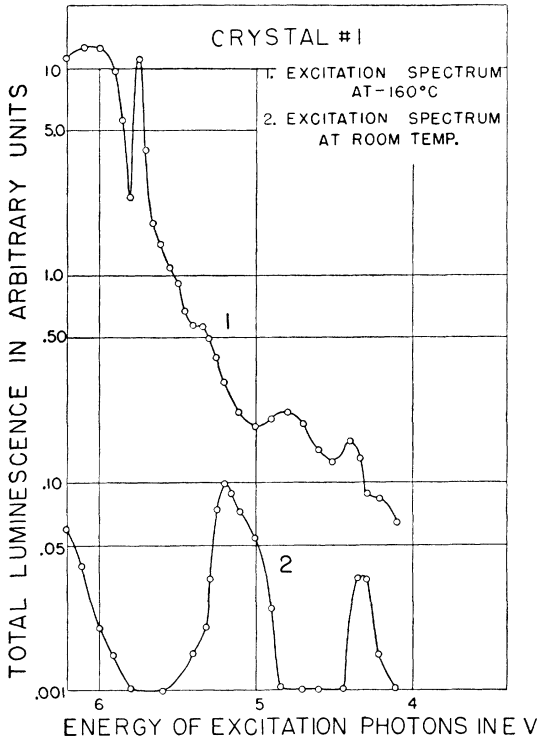

FIG. 4. Excitation spectrum of a potassium iodide crystal at −160°C and room temperature. The measurements were made using a constant number of excitation photons per second. Small thallium excitation bands appear at 4.35 ev and 5.20 ev at room temperature.

Excitation with 5.8-ev light also leads to similar emission spectra for the two crystals. When excited with 5.75-ev light crystal number 1 emitted light in a band with peak at 3.3 ev and half-width 0.7 ev, just as with 5.9-ev excitation. This is shown in curve 3, Fig. 7. Crystal number 2 behaved differently upon excitation with 5.75-ev light. The emission band for this case, shown in curve 3, Fig. 8, has its peak at 3.1 ev with a half-width of 0.5 ev. Excitation with 2.65-ev light led to about the same emission spectrum for both crystals.

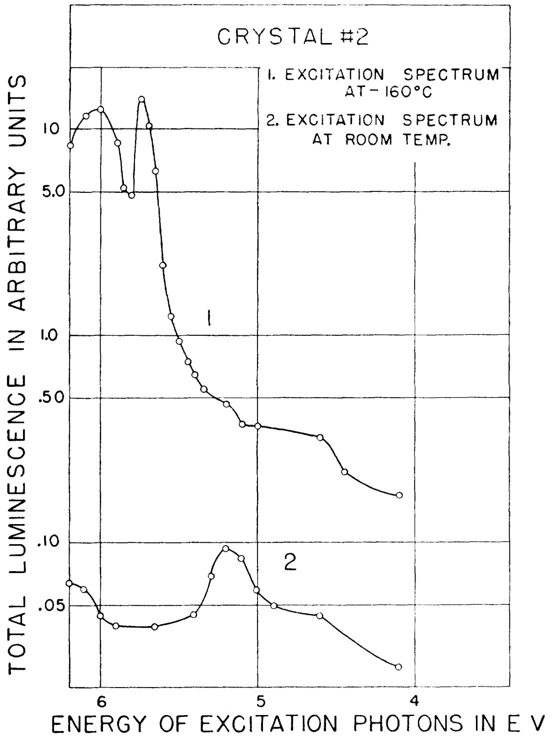

FIG. 5. Excitation spectrum of a crystal of potassium iodide grown from reagent grade material and crystallized twice. The same number of excitation photons per second was used as in the case of crystal 1.

The emission spectra for crystal number 3 is shown in Fig. 9. Excitation of this crystal with 5.9-ev light caused emission in a band with peak at 3.3 ev, as in the case of crystals 1 and 2. However, the band characteristic of crystal number 3 has a half-width of 0.8-ev, instead of 0.7 ev, and appears to have a shoulder at about 2.95 ev. This may indicate the presence of an additional band with peak at about 2.9 ev. When crystal number 3 was illuminated with light absorbed in the thallium excitation bands, the emission spectrum given in curves 1*B* and 2*B* of Fig. 9 was obtained. These show the well-known thallium emission bands reported by many previous workers.[6] It is to be noted that the main thallium emission band lies at 2.9 ev. Thus curve 1*A* of Fig. 9 could be explained by assuming that part of the energy absorbed in the fundamental band gives rise to the emission characteristic of pure potassium iodide and part is transferred to thallium ions causing them to luminesce. The fact that the emission bands produced by excitation with 5.8-ev and 5.75-ev light lie to the red of the emission bands produced by the same excitation of crystals 1 and 2 is in agreement with the above hypothesis. Excitation of the crystal with 5.65-ev light gave rise to an emission band almost indistinguishable from the main thallium emission band, as is shown by curve 4*A* in Fig. 9.

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[6] W. von Meyren, Z. Physik **61**, 321 (1930).

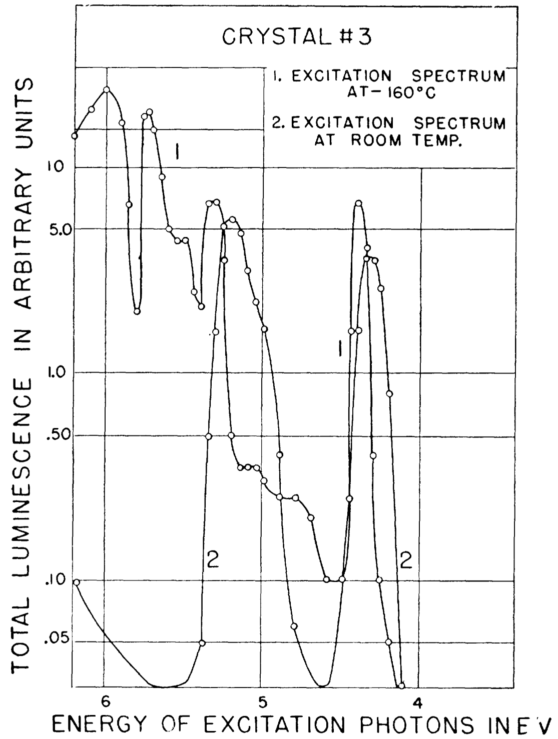

FIG. 6. Excitation spectrum of another potassium iodide crystal which contained more thallium. Again a constant number of excitation photons per second was used and the number was the same as in the case of crystal 1.

3. Quantum Yield

The quantum yield of crystal 1 for an excitation energy of 5.75 ev was found to be 1.18. The yield of crystal 2 for the same excitation energy was 0.93. These numbers were calculated under the assumptions noted in Sec. II. They are probably good to no better than a factor of 2.

An independent estimate of the quantum yield may be obtained using the excitation spectrum and optical absorption spectrum of crystal 3. About 15% of the light was absorbed in the thallium excitation band at 4.4 ev while we assume that 60% of the light was absorbed in the fundamental band excitation peak at 5.75 ev. The ratio of the heights of these excitation peaks is 2.9. The quantum yield for thallium luminescence is supposed to be 1. If we assume this, the fundamental band luminescence had a quantum yield of 0.73, which agrees with the direct measurements within the expected error.

IV. CONCLUSIONS

The experiments described above are to be taken as preliminary to a more thorough investigation of the low-temperature luminescence phenomena in the alkali halides. The following comments on the present work will indicate the type of experiments this investigation will include.

One of the main points of interest in the interpretation of the results of these experiments is whether or not the low-temperature luminescence is characteristic of the pure material or is dependent upon the presence of some impurity or defect in the crystals. The author feels that the emission found when the crystals were irradiated with 5.9-ev light is a property of the pure KI lattice. The reasons behind this tentative conclusion are as follows.

The three crystals used had different histories and the optical absorption measurements in the region of the fundamental band tail indicate that the crystals contained different amounts of impurities and defects. For example, thallium was present in different amounts in crystals 1 and 3 and perhaps in 2. Despite this, all three crystals showed very similar emission spectra when irradiated with 5.9-ev light and the quantum yield for the three crystals was the same within experimental error.

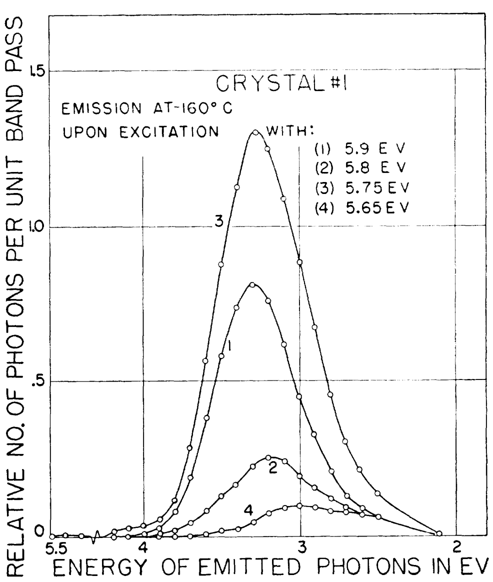

FIG. 7. Emission spectrum of crystal 1. Note that the measurements were made over the region from 2.10 ev to 5.50 ev.

From the optical absorption data it appears that crystal 1 was the most pure of the three. It is significant that for this crystal, the emission bands produced upon illumination with 5.9-ev light and 5.8-ev light were the same as far as position is concerned. In crystals 2 and 3, illumination with 5.8-ev light produced emission bands lying to the red of the emission band excited with 5.9-ev light. But it is known that the absorption of light in the long-wavelength tail of the first fundamental absorption band depends strongly on the purity and perfection of the crystal. Hence, it is to be expected that the luminescence produced by illumination in the tail will also depend on the purity and perfection of the crystal. If the KI itself also luminesces independently of any impurities or defects, then the purer the crystal the more the tail luminescence will resemble the luminescence produced by illumination near the peak of the fundamental band, as is shown for crystal 1.

At any rate, it is clear that the initial process leading to luminescence is one in which a photon is absorbed at a negative ion in the lattice and, therefore, the experiments reported on here may have an important bearing on the processes by which such absorbed energy can be transmitted through the alkali halide lattice. This is true whether or not the luminescence is due to the pure crystal. If defects or impurities are necessary for the observed emission to occur, then presumably the energy of an excited negative ion is transferred by some means to the defect or impurity and a study of the quantum yield of luminescence as a function of impurity or defect concentration may give some idea of the energy transfer mechanism. This type of experiment might be made to yield the first definite evidence of the existence of an "exciton" in the alkali halide lattice, for example.

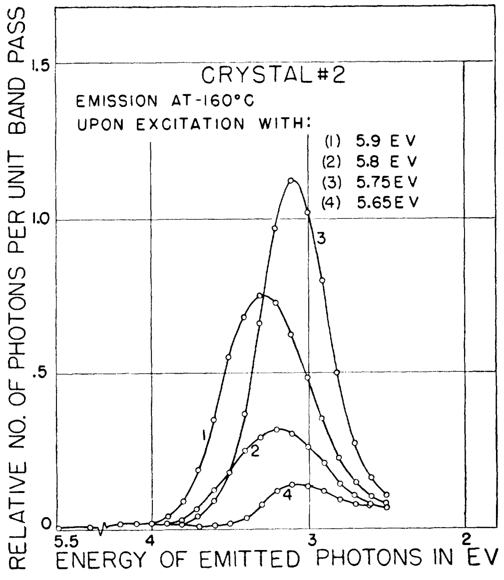

FIG. 8. Emission of crystal 2.

If the luminescence reported on here is due to the pure alkali halide lattice, as we suspect, then other interesting experiments are possible. It is known that F-centers can be ionized by irradiation in the fundamental band of these crystals. This process must compete with photon emission for the energy of the absorbed quanta. Hence pure crystal luminescence should be quenched by the presence of a sufficient concentration of F-centers. How far does the F-center have to be from the initial site of absorption before it can receive the energy of the excited negative ion? Again, an answer to this question would yield some information as to the energy transfer mechanism. We, therefore, would like to study the quenching effect as a function of F-center concentration.

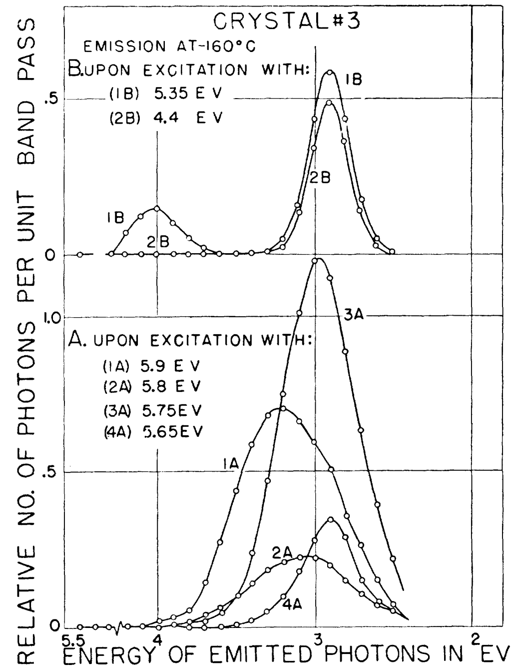

FIG. 9. Emission of crystal 3. The thallium emission spectrum is included for comparison (curves $1B$ and $2B$).

Also, it may be that an excited negative ion would prefer to give its energy to some impurity center such as thallium if the impurity were present in sufficient concentration. A quenching of the pure crystal luminescence and the appearance of induced thallium luminescence might be observed in this case as the concentration of thallium is increased.

It is hoped that it will be possible to report on the results of experiments of this nature in the near future.

V. ACKNOWLEDGMENTS

The author wishes to express his thanks to Dr. David Dutton and Dr. David Dexter for their many contributions to this investigation. He is also indebted to Dr. L. Apker for an interesting discussion and information concerning the reflection loss to be expected from single potassium iodide crystals and to Dr. G. Chiarotti who provided one of the crystals used in this experiment.