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Fluorescence and Reflection Spectra of NaI Single Crystals*

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The fluorescence emission and excitation, reflection, and transmission spectra of 22 different NaI crystal samples grown in crucibles of Pt or quartz under atmospheres of N_2 or H_2 or H_2 plus I_2 and in some cases containing stoichiometric excess of Na or I_2 or containing various concentrations of Tl, have been explored from 2.5 to 8 ev. At −190°C an emission band centered at 295 mμ (4.20 ev) was observed in all but the one sample which contained the highest Tl concentration, 0.1 mole %. Another emission band at 375 mμ (3.31 ev) was found to be strongest in crystals containing excess I_2. A 425 mμ (2.92 ev) emission appeared strongly in all crystals containing Tl, but a 325 mμ (3.82 ev) band appeared only in the one crystal with 0.1 mole % Tl. With excitation energy below 5.5 ev the different emission bands arise from discrete excitation bands. With excitation energies above 5.5 ev up to 8 ev the emission was primarily in the 295-mμ band until Tl concentration reached 0.05 mole % where the 425-mμ band and 295-mμ band became approximately equal. Maxima in reflection spectra coincide closely but not exactly with published maxima in the absorption spectra of NaI evaporated films. An inflation, not seen in the published absorption spectra, appears at 5.62 ev in the reflection spectrum at −190°C. Coincidental with the lowest energy maximum in the reflection spectrum at 5.59 ev the excitation spectra for both 295-mμ and 425-mμ emission exhibit minima too strong to be accounted for by reflection loss. At excitation energies of 5.7 ev and above, luminescence quantum efficiency is greatest for an illuminating angle of incidence of 45° whereas at lower energies no definitely preferable incidence angle was found. Also with higher exciting energies it was found that the emission was strongest on the axis of illumination. With exciting energies below 5.5 ev the emission was isotropic.

I. INTRODUCTION

Quite apart from its usefulness as a detector of high-energy radiation, the NaI crystal offers an interesting vehicle for the study of solid state phenomena. Under some circumstances, it exhibits fluorescence of high quantum efficiency, the excitation bands of which may be correlated with optical absorption bands, yielding a powerful tool for the investigation of impurity and other defect centers in solids and of energy transport mechanisms.

NaI has received considerable experimental attention. However, because of its practical application to the nuclear physicist, most of the investigations have been restricted to its scintillation characteristics. In addition, investigations of the ultraviolet absorption spectrum of evaporated films,[1–4] the absorption spectrum of thallium doped single crystals,[5] *V* center absorption bands in single crystals,[6] fluorescence in unactivated[7] and in thallium activated[8] crystals of NaI have been reported.

The investigation to be reported here consisted of a series of measurements on a number of different NaI crystals conducted in the temperature range +20°C to −190°C. The crystals were illuminated with a high resolution vacuum monochromator working in the range from 4 ev to 8 ev while the emission spectra were analyzed with a second monochromator working in the range of 2.5 ev to 5 ev. Measurements were made of the fluorescence emission and excitation spectra, reflection spectra, and optical transmission spectra of these single crystals. Approximately 350 spectra were run on a total of 22 different crystal samples. In this group were crystals grown in crucibles of platinum, quartz, or pyrex, crystals grown in atmospheres of nitrogen or hydrogen or hydrogen plus iodine, crystals grown in a horizontal zone refining furnace, crystals to which a stoichiometric excess of sodium or iodine was added by diffusion, and crystals grown with various concentrations of thallium. While there is, to some extent, an overlap with previous investigations, the present work is felt to be for the most part new. The work is of higher precision and goes farther into the ultraviolet than previous optical measurements on single crystals of NaI.

The results of specific measurements, selected because they are typical and illustrate one or more significant characteristics, are presented in the figures. Reflection measurements are presented separately as a group as are the spectra of the emission bands. However, excitation spectra and transmission spectra applicable to a specific crystal at a specific temperature are for the most part grouped together in one figure.

The discussion, particularly of the fluorescence, is organized more or less orthogonally to the organization of the figures. For example, attention is centered on a particular emission band while the conditions of crystal preparation, temperature, and excitation spectra producing this particular emission band are examined.

This investigation was primarily experimental and no attempt at a sophisticated theoretical treatment of the results will be made in this article. Some theoretical implications are discussed qualitatively.

II. EXPERIMENTAL

1. Preparation of Crystals

All crystals were grown from the melt using Mallinckrodt analytical reagent. The majority of the crystal

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* Supported in part by the U. S. Atomic Energy Commission.

† A Subsidiary of Radiation Incorporated.

[1] R. Hilsch and R. W. Pohl, Z. Physik **59**, 812 (1930).

[2] W. Martienssen, J. Phys. Chem. Solids **2**, 257 (1957).

[3] K. Teegarden, Phys. Rev. **108**, 660 (1957).

[4] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).

[5] R. Hilsch, Proc. Phys. Soc. (London) **49**, 40 (1937).

[6] Y. Uchida and Y. Nakai, J. Phys. Soc. (Japan) **9**, 928 (1954).

[7] W. Van Sciver and R. Hofstadter, Phys. Rev. **97**, 1181 (1955).

[8] W. Van Sciver, IRE Trans. on Nuclear Sci. **NS-3**, 39 (1956); Stanford University Technical Report HEPL-38 (unpublished).

samples were cleaved from 15 pound ingots grown in a Stockbarger[9] type of furnace which is provided with a vacuum tight liner of opaque fused silica.

To minimize decomposition of NaI, precautions are taken to remove oxygen and water at low temperature. However, NaI must be heated to at least 65°C to release H_2O from $NaI \cdot 2H_2O$. In practice the furnace is slowly warmed to 200°C over a period of approximately four hours. During this initial warming its cylindrical inner chamber containing a crucible loaded with NaI is alternately evacuated and refilled with nitrogen or hydrogen.

After a final evacuation at 200°C the chamber is filled with nitrogen or hydrogen at 760 mm Hg pressure. The temperature of the upper half of the furnace is stabilized at 675°C and the lower half at 625°C. Crystallization is achieved by lowering the crucible at a rate of approximately $\frac{1}{2}$ inch per day. When the crystal is fully grown the furnace must be opened, the crucible inverted, and the crystal melted out of it. Although the actual melting out operation is conducted in an inert or reducing atmosphere, the brief exposure of the crystal to air during the time the furnace is opened does result in some dissociation of the surface crystalline material as evidenced by the release of iodine vapor.

Therefore, crystals produced by this method must contain some hydroxide as a result of this exposure to air, through the reaction: $4NaI+O_2+2H_2O=4NaOH+2I_2$. The I_2 evaporates, but the NaOH may remain on the crystal surface to diffuse in at a later time during the annealing period. Some crystals were also produced in a small Stockbarger type of furnace of $1\frac{1}{2}$ inch bore diameter. This furnace has a transparent quartz envelope in which a quartz crucible is used. Several attempts were made to produce crystals free from hydroxide by maintaining an excess pressure of hydrogen or hydrogen plus iodine in order to inhibit hydroxide formation. (The quartz crucible is a very sensitive indicator for hydroxide, since it is severely etched by it.) In spite of this precaution and in spite of the fact that the crystal was not exposed to air, it being allowed to cool in the crucible, we were unable to produce hydroxide-free crystals in this way. The third furnace, horizontal in form and consisting of a quartz tube with moving external heaters, was used in the manner of a horizontal zone refining furnace similar to the type used in the purification of silicon and germanium. This furnace was arranged to permit a continuous flow of iodine and hydrogen over the sodium iodide during the entire warming and growing process. In it crystals were produced which did not etch nor, in fact, adhere to the quartz crucible in which they were grown. It was thus indicated that these last crystals were free from hydroxide.

Crystals to be treated with Na or I_2 vapor to provide a stoichiometric excess of one of these were handled as follows: A freshly cleaved piece of crystal, grown in quartz under a nitrogen atmosphere, was placed in a previously baked out quartz tube along with either a freshly cut piece of Na, or a crystal of iodine. The tube was evacuated and sealed off. Then, by judicious shaking the NaI crystal could be gotten to one end and the Na or I_2 to the other. The quartz tube was then placed in a small horizontal furnace which was adjusted to give 500°C in the region of the crystal and at the other end, 200°C for I_2 or 500°C for Na. The temperature of the furnace was maintained for 20 hours and then cooled to room temperature over approximately a two hour period. Both loading and subsequent breaking of the quartz tube to regain the NaI crystal were carried out in a dry box.

Crystals containing Tl were prepared by mechanically mixing TlI powder with NaI powder prior to growing the crystal by the method described in the first part of this section. Tl concentration was determined by chemical analysis of dissolved crystal samples with an accuracy of ± 0.01 mole % Tl.

2. Apparatus for Measurement

All measurements, transmission, reflection, and fluorescence, were made in a single experimental setup as follows: A freshly cleaved crystal was clamped under moderate spring pressure to the bottom of a metal Dewar which could be inserted in the top of a vacuum tight chamber. The crystal to be examined could thereby be placed on the perpendicularly intersecting axes of four ports in the chamber. Two of these ports are fitted with Corning quartz windows, a third with Corning quartz lenses which are the entrance collimator for a 250 mm Bausch & Lomb monochromator used as an analyzer for the fluorescence. Windows of these three ports are interchangeable. The fourth port is fitted with a calcium fluoride lens to image the incident light from the illuminating monochromator on the crystal. The illuminating system consists of a Jarrell-Ash 500 mm focal length concave grating vacuum monochromator of the Seya Namioka type and a Hanovia high pressure hydrogen lamp fitted with a calcium fluoride window and maintained at a constant hydrogen pressure of 6 mm Hg. The lamp was operated at 13 amperes which required approximately 1500 volts ac supplied by an electronically stabilized source. A plastic dry bag with rubber gloves was fitted to the top of the cryostat so that crystals could be freshly cleaved and mounted on the clamp of the Dewar without exposure to moist air. The dew point of the air in the bag could be maintained at −50°C by means of an external continuously circulating drying system. The cryostat was furthermore fitted with a razor blade actuated through a Wilson seal to permit cleaving the crystal face while in place. It was found that results were indistinguishable whether the crystal was freshly cleaved and then inserted in the apparatus or cleaved in a vacuum after insertion. The

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[9] D. C. Stockbarger, Rev. Sci. Instr. 7, 122 (1936).

cryostat was evacuated by a diffusion pump and mechanical fore pump protected between the diffusion pump and cryostat with a liquid nitrogen trap. In spite of this, it was found that over a period of 24 hours a noticeable deterioration of the crystal face would be observed in terms of its excitation spectrum and/or reflection spectrum. The effect was most severe if the crystal had been cold and then permitted to warm up again. However, experimental measurements ranging over a period of several hours could be made without detectable deterioration.

By sliding or twisting the Dewar, the crystal sample could be placed in or out of the illuminating beam or the angle of incidence adjusted without disturbing cryostat vacuum.

Detection of transmitted or reflected illumination was accomplished with an RCA-6903 quartz face photomultiplier. Its useful range extended to 7.3 ev in the vacuum ultraviolet. Detection of fluorescent light after analysis by the 250 mm monochromator was accomplished with an RCA-7200 quartz envelope photomultiplier with a metal-backed photocathode. To reduce noise this tube was cooled to liquid nitrogen temperature.

Direct current from the photomultipliers was measured with a General Radio Electrometer Type 1230A driving a 10-mv chart recorder. Both the illuminating monochromator and the analyzing monochromator were fitted with synchronous drive motors. Since a continuous recording of data was made, no points appear in the spectrum figures.

Calibration of sensitivity versus wavelength for the analyzer system (250-mm monochromator and RCA-7200 phototube) was accomplished by comparison with a thermopile. Sodium salicylate sprayed on the inside of one of the quartz windows was used as a phosphor to determine the intensity spectrum of the illuminating system. This provided a correction curve which was applied to measured excitation spectra.

It was assumed that sodium salicylate has constant quantum efficiency.[10] The validity of this assumption is doubtful but there was no readily available alternative since the available thermopile was not sufficiently sensitive. In any case the same curve was applied to all excitation spectra, so that even if absolute values are in error, the differences in curve shapes between different figures indicate real differences in the phenomena.

III. DISCUSSION

1. Reflection Spectra

The reflection spectrum of NaI single crystals at −190°C is found to be qualitatively very similar to the absorption spectra of evaporated films of NaI,[1–4] as optical theory[11] predicts it should be. The amplitudes, being in different units, are not comparable, but the locations, with respect to wavelength or photon energy, of the peaks or maxima in the reflection spectrum agree closely with the published results for absorption spectra. The reflection spectrum of NaI single crystals at −190°C exhibits one feature, an inflection at 5.62 ev, which does not appear in the published results for the absorption spectra of NaI evaporated films. Reflectivity of the lowest energy reflection peak, at 5.59 ev, reaches a maximum value slightly in excess of 50%.

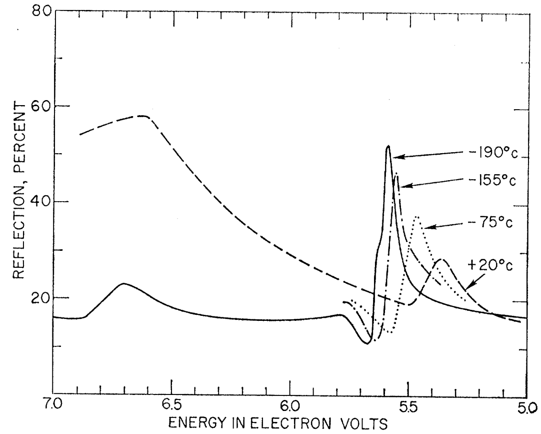

FIG. 1. The reflection spectra of an NaI single crystal grown in a Pt crucible under an N_2 atmosphere. Illuminating angle of incidence 45°.

Figure 1 shows the reflection spectra for an NaI crystal grown in a Pt crucible under an N_2 atmosphere at −190°C, +20°C, and the region of the first reflection peak for two intermediate temperatures. These spectra were all taken with the angle of incidence at 45° to the crystal face (110 direction), and the detector located at 90° to the direction of incident photons. The incident intensity was measured by moving the detector into the direct beam. Some measurements of normal incidence reflection were made by the use of a quartz plate mounted at 45° in the illuminating beam path. Light reflected by the crystal was then partially reflected by the quartz plate to the detector. Comparison of the spectra showed that qualitatively they were very similar, the peaks all appearing in exactly the same place, but some discrepancies in amplitude were observed. However, the low reflectivity of the quartz plate made accurate quantitative comparison impossible.

Comparison of the reflection curve for −190°C with that given by Martienssen[2] for NaI at −253°C shows a remarkable agreement for the location of the peaks. Martienssen gives 5.59 ev for the first absorption peak and 6.72 ev for the second peak. He gives the step at 5.80 ev. Within the experimental accuracy of the two measurements, the agreement is exact. However, unless the temperature dependence of the peak locations is zero in the range of −253°C to −190°C, there is, in actuality, a discrepancy. Teegarden[3] has given for NaI at −180°C the value 5.575 for the first peak and more

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[10] K. Watanabe and E. Inn, J. Opt. Soc. Am. **43**, 32 (1953).

[11] H. Y. Fan, *Methods of Experimental Physics*, edited by L. Marton (Academic Press, New York, 1959), Vol. 6, Part B, Chap. 10, p. 249 ff.

recently Eby *et al.*[4] give 5.56 at −193°C. For the second peak and the step, the agreement is good in all cases.

The illuminating monochromator used in the measurements presented here had a dispersion of 17 A per mm. At 200 μ slit width, the value used in reflection measurements, this converts to a band pass of 0.0086 ev at 5.6 ev. The instrument was adjusted and calibrated to an accuracy of $\pm\frac{1}{2}$ A or approximately 0.0013 ev in this wavelength region. It appears that there is a definite discrepancy between the location of the first peak as found by reflection from a crystal and that as found in the absorption spectrum of an evaporated film of the same material. However, it should be pointed out that temperature measurements on crystals or films supported in optical beams are difficult and somewhat unreliable in view of the fact that they are subject to heating by the incident beam and their thermal conductivity is low.

An inflection on the high-energy side of the first reflection peak appears at 5.62 ev. This is not shown in any of the reported absorption measurements of evaporated films. A band pass of no greater than 0.01 ev was required to resolve the inflection. However, Eby *et al.*[4] used approximately this value in making their evaporated film absorption measurements and should have resolved the inflection if it is present in the sodium iodide film absorption band. Possibly it is caused by a surface defect of the single crystal.

The effect of reflection in reducing absorbed exciting radiation and its effect on the shape of the observed excitation spectrum is illustrated in Fig. 3.

2. Optical Transmission Spectra

All of the crystals used in these measurements were cleaved to 1 mm±0.1 mm. The data is presented in Fig. 4 through 14 in the form of per cent transmission and the losses due to surface reflection are not taken into account. In spite of its unconventionality and lack of sophistication, it is the most practical way for the information to be presented. It makes possible the presentation of transmission spectra on the same figure with the excitation spectra for a given crystal at a given temperature. Some characteristics of the transmission spectra seem to be worthy of separate emphasis at this point. Before entering discussion of the more complex fluorescence emission and excitation spectra, an attempt is made to identify the defect or impurity centers responsible for two of the absorption bands (corresponding to depressions in the transmission spectra).

The crystal shown in Fig. 4 shows that the transmission cut-off occurs at 5.5 ev and that there is not much of a tail in the transmission, or absorption, spectrum. The $1/e$ transmission corresponding to an absorption coefficient of one inverse millimeter appears at about 5.42 ev. Two inflections, one at 5.3 ev and the other at 4.8 ev, are apparent in this curve and correspond to weak absorption bands. Comparison of this curve with that of Fig. 9 for NaI (I_2) at −190°C shows that the stoichiometric addition of iodine enhances the 4.8-ev band whereas that at 5.3 ev remains unaffected. It appears that the 4.8-ev absorption band may correspond to a *V* band. Uchida and Nakai[6] did not observe this band in NaI, but it does correspond closely with the highest energy absorption band which they observed in KI (4.77 ev at +20°C). They produced this band, along with two lower energy ones, in KI by heating the crystal in iodine vapor. The two lower energy absorption bands in KI were also produced by passing a current from a sharply pointed anode into the crystal. However, this latter method failed to produce the 4.77-ev band, and the authors concluded that the latter may not be a *V* band.

The energy difference between the 5.3 ev and the first absorption peak is 0.29 ev which when compared with experimental and theoretical results for KBr and KI[12] suggests that this band at 5.3 ev may be a β band corresponding to the presence of *F* centers in the crystal. Figure 5 illustrates the result when an attempt was made to enhance the *F*-center population of a sodium iodide crystal by heating it in sodium vapor. The transmission of this crystal reached essentially zero at 5.3 ev and no transmission was detectable at shorter wave-

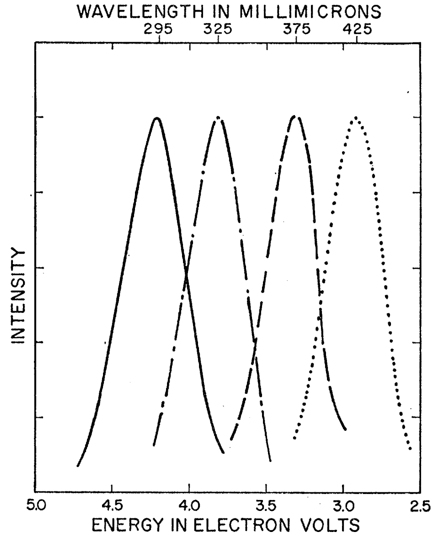

FIG. 2. Luminescence emission bands observed in NaI single crystals at −190°C. The 295-mμ band appeared in all crystals containing 0.05 mole % Tl or less at −190°C. The 325-mμ band appeared only in a crystal containing 0.1 mole % Tl. The 375-mμ band appeared with greatest intensity in crystals with a stoichiometric excess of I_2. The 425-mμ band appeared in all crystals containing Tl and in no others. The last two bands have approximately constant quantum efficiency between −190°C and +20°C. The intensity scale is arbitrary and all curves are arbitrarily shown with equal maxima.

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[12] C. J. Delbecq, P. Pringsheim, and P. Yuster, J. Chem. Phys. **19**, 574 (1951); **20**, 746 (1952). W. Martienssen, Z. Physik **131**, 488 (1952); Nachr. Akad. Wiss. Göttingen **111** (1952). W. Martienssen and R. W. Pohl, Z. Physik **133**, 153 (1952); F. Seitz, Revs. Modern Phys. **26**, 7 (1954); F. Bassani and N. Inchauspé, Phys. Rev. **105**, 819 (1957).

lengths. Consequently, it is not possible to say whether the hypothetical β band was actually enhanced and merged with a fundamental absorption or if some other, perhaps colloid, band was produced in the crystal which made it simply opaque in this region. In any case, the *V* band previously appearing at 4.8 ev was completely wiped out by exposure to sodium.

Optical absorption bands in crystals containing thallium correspond exactly to excitation bands for luminescence. When appropriate they are discussed along with the luminescence.

3. Luminescence Emission and Excitation Spectra

Figure 2 shows the four emission bands found in sodium iodide at liquid nitrogen temperature. Their centers are located at: 4.20 ev, 3.82 ev, 3.31 ev, and 2.92 ev. Their shapes and widths are similar and their spacing surprisingly uniform. However, the significance, if any exists, of these rather uniform characteristics is not understood. The intensity scale of Fig. 2 is arbitrary, all curves having been plotted with equal maxima. However, there was found at least one condition of crystal preparation, temperature, and photon excitation energy which produced a maximum quantum efficiency which was equal, within ±10%, for each of these four bands. It is felt that this maximum probably corresponds to something close to 100% quantum efficiency although the calibration was not sufficiently accurate to assure this. For the purposes of the following discussion, the emission bands will be simply designated by their wavelengths, i.e., 295 mμ (4.20 ev), 325 mμ (3.82 ev), 375 mμ (3.31 ev), and 425 mμ (2.92 ev). A summary of the characteristics of the NaI fluorescence is given in Tables I and II.

Figures 3 through 14 show the excitation spectra for these bands under various conditions of crystal preparation and temperature. All figures are corrected to show quantum efficiency in terms of constant incident flux, while Fig. 3 also shows quantum efficiency for constant absorbed flux, obtained by correcting for reflectivity. The absolute value of quantum efficiency indicated on the figures is probably accurate to a factor of 2. The shape of an individual curve is probably accurate to 5% of its value at any point, but this, it must be born in mind, is not absolute but referred to sodium salicylate.

TABLE I. NaI fluorescence not requiring the presence of thallium in the crystal.

Emission band	Excitation band	Conditions for detectability
295 mμ (4.20 ev)	5.3 ev	crystal optically clear in 5.3-ev region; tempera- −75°C or lower
295 mμ (4.20 ev)	5.5 ev	Crystal temperature −155°C or lower; thallium content not more than 0.05 mole %
295 mμ (4.20 ev)	5.7 ev and above	
375 mμ (3.31 ev)	4.80 ev (20°C)	Stoichiometric excess of iodine and no detectable thallium in crystal
375 mμ (3.31 ev)	5.26 ev (20°C)	
375 mμ (3.31 ev)	4.85 ev (−190°C)	
375 mμ (3.31 ev)	5.47 ev (−190°C)	

TABLE II. NaI fluorescence depending on the presence of thallium in the crystal.

Emission band	Excitation band at −190°C	mole % of thallium required for detectability	Probable corresponding KI absorption band (*s*) as observed by Yuster & Delbecq[a]
325 mμ (3.83 ev)	4.07 ev	0.1	4.23 and 4.27 ev
425 mμ (2.92 ev)	4.26 ev	less than 0.025	4.40 ev
325 mμ (3.83 ev)	4.82 ev	0.1	4.92 and 4.96 ev
425 mμ (2.92 ev)	4.97 ev	<0.025	5.08 ev
325 mμ (3.83 ev)	5.05 ev	0.1	not observed
425 mμ (2.92 ev)	5.1 ev and above	<0.025	5.32 ev and above

[a] See reference 14.

Some of the curves of excitation spectra exhibit an almost square flat maximum as though the limit of detecting system response was being exceeded. Actually, the intensity of emission was many orders of magnitude below the saturation limit for the detecting system. Rather, the flat tops of excitation spectrum curves more likely represent regions where the quantum efficiency approaches 100%.

295 mμ *(4.20* ev*) band*

The most significant characteristic of the 295-mμ emission band is its persistence. It appears at liquid nitrogen temperature in all crystals with the exception of the one most heavily doped with thallium.

It has an excitation band centered at 5.3 ev which appears in all of the crystals except those doped with

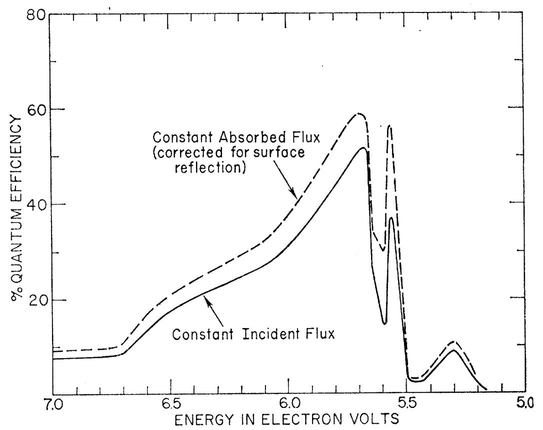

FIG. 3. Excitation spectrum for 295 mμ (4.20 ev) emission in an NaI crystal at −190°C grown in Pt under an N_2 atmosphere. Illuminating angle of incidence 45°. Solid curve corrected for constant incident flux. Dashed curve corrected for reflectivity to give excitation spectrum for constant absorbed flux.

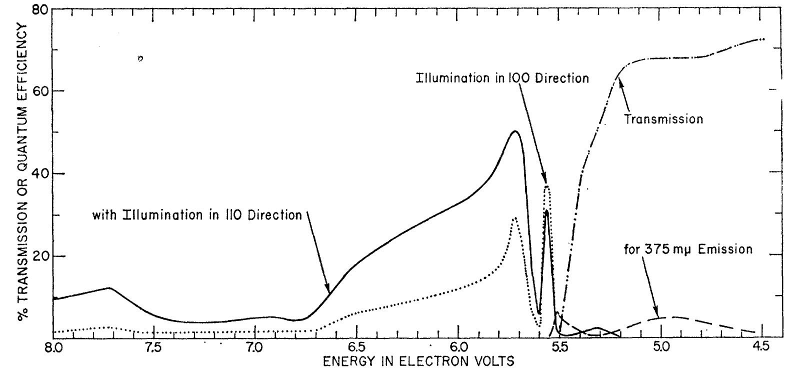

FIG. 4. Excitation and transmission spectra of an NaI crystal grown in quartz under an H_2 atmosphere. With respect to the 295 mμ (4.20 ev) emission the solid curve is for 45° illuminating angle of incidence; the dotted, for 5° angle of incidence. In all case luminescence was transmitted through the crystal to analyzer input optics at 90° to illuminating beam. The rise in quantum efficiency at 7.7 ev coincides with a tenfold rise in illuminator intensity. When illuminator intensity was reduced, the excitation curve flattened out in this region.

Na or Tl. The 5.3-ev band varies somewhat in strength with different crystals, but where it is moderately strong it appears to be essentially temperature independent in the range of $-75°C$ to $-190°C$. At temperatures above $-75°C$ it becomes merged with one of the excitation bands for the 375-mμ emission (see below). The 5.3-ev excitation band appears to be a volume rather than surface band since it is associated with an inflection in the optical transmission curve and is absent when, because of addition of other impurities, the crystal is opaque in this region.

The 295-mμ band is excited by a continuum beginning at 5.5 ev and extending to at least 8.0 ev (the high-energy limit of the measurements). Its quantum efficiency is greatest immediately above and below the first absorption or reflection peak with a deep minimum at the peak. The quantum efficiency diminishes to make a rather steep drop on the low-energy side of the second exciton peak at 6.7 ev. Measurements made at 7.7 ev using different incident photon flux intensities varying over a range of 8:1 indicate an increasing quantum efficiency with increasing flux. However, similar measurements made near the low-energy end of the band at 5.7 ev showed the quantum efficiency to be independent of incident flux intensity. At the lowest energy end of the excitation continuum (5.5 ev) it is found that the quantum efficiency reaches a broad indefinite maximum when the crystal is oriented close to normal incidence for the illuminating photons; namely, an illumination in the 100 direction. However, on the high-energy side of the first reflection peak, the greatest quantum efficiency is found with the crystal at 45° to the incident light (illumination in the 110 direction), and the effect becomes more marked as the incident photon energy increases. In addition to the dependence of total quantum efficiency on the direction of incident light, it was also observed that in the high-energy end of the continuum, the emitted light is primarily in the forward direction, whereas at the low-energy end (5.5 ev) the emitted light was primarily perpendicular with a small forward component of approximately 5°. In none of the fluorescence excited with energies of less than 5.5 ev was any preferable direction found, either for the incident or emitted radiation.

The curious characteristics of preferred illuminating angle of incidence and of nonisotropic emission for excitation energies above 5.5 ev were discovered quite by accident. Once observed, the phenomena were looked for in several crystal samples, and although the apparatus was not suited to precise measurement of the

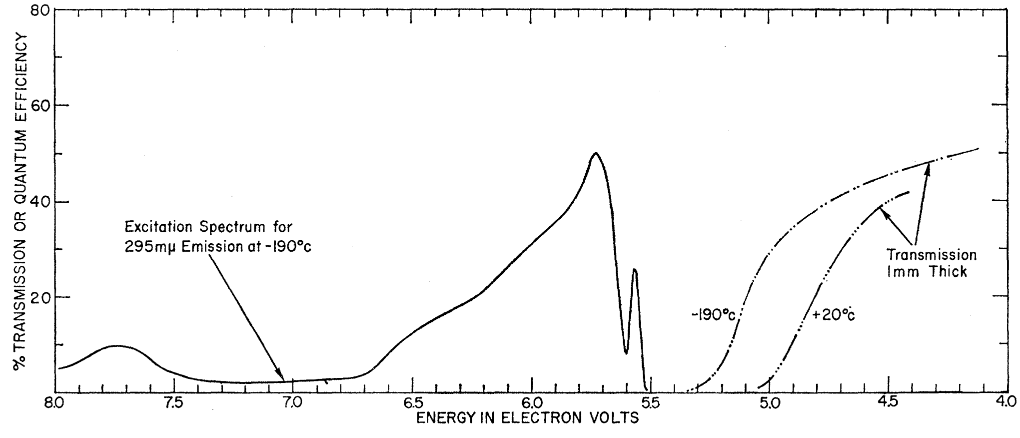

FIG. 5. Excitation and transmission spectra for an NaI crystal grown in Pt under an N_2 Atmosphere with stoichiometric excess of Na subsequently diffused in at 500°C.

angles involved, there remains no doubt that the effects are real. Their possible significance is discussed below in the section on energy transport.

The excitation continuum for the 295-mμ emission exhibits a strong temperature dependence. Figure 15 illustrates the temperature dependence in the range $-150°$ to $-190°C$ for excitation of 5.7 ev and also illustrates the temperature independent behavior of the 5.3-ev excitation band.

Examination of the results strongly indicates that this band is associated directly with the excitation band found at 5.3 ev and the inflection in the optical transmission curve also found at that region. Although this is not the strongest excitation band for the 295 emission, it has the attractive feature of being nearly temperature independent, which in general seems to characterize principal excitation bands in phosphors. Its weakness, as compared with the excitation by 5.5- or 5.7-ev photons may be explained by the relative weakness of this band as an optical absorption band in all of the measurements made and by its complete submersion in much stronger absorption in crystals doped with sodium or thallium. Whether or not this band is actually a β band associated with an *F* center remains an open question. Its location at $-190°C$ suggests that this is so. However, it fails to shift to lower energy at higher temperatures. Also the failure to arbitrarily produce it or enhance it leaves a considerable question open. Still the failure to enhance this band by heating the crystal in sodium should not be taken as evidence against its being caused by *F* centers. The small size of the sodium ion as compared with the iodine ion makes it difficult to contemplate the production of *F* centers in this manner.

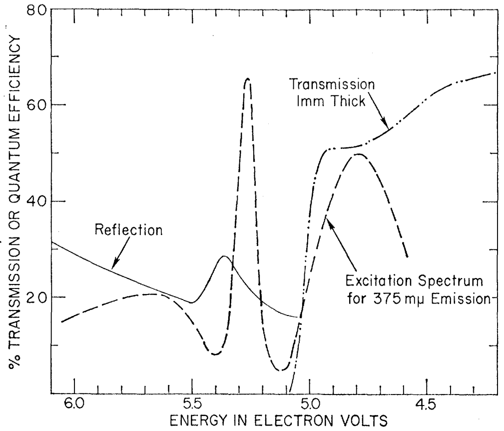

FIG. 6. Excitation and transmission spectra for an NaI crystal grown in Pt under an N_2 atmosphere with stoichiometric excess of I_2 diffused in at 500°C crystal temperature and approximately 1.4 atmospheres pressure of I_2. Measured at $+20°C$.

The possibility that the 5.3-ev absorption and excitation band is caused by hydroxide in sodium iodide was considered since as was indicated in the section on crystal preparation, essentially all crystals must have contained some hydroxide. Rolfe[13] has examined hydroxide absorption bands in KBr, KCl, and NaCl. In the first of these it appears at 5.77 ev, or about 1.0 ev below the first absorption peak. If roughly the same energy shift should apply in sodium iodide, this could not cause the 5.3-ev band. Experimentally, this was confirmed by measurements on the hydroxide-free crystals produced in a continuously flowing atmosphere of hydrogen and iodine. With respect to the 5.3-ev band, these crystals were very similar to the crystals grown in nitrogen, and other bands only indicated a stoichiometric excess of iodine. Furthermore, crystals heated in

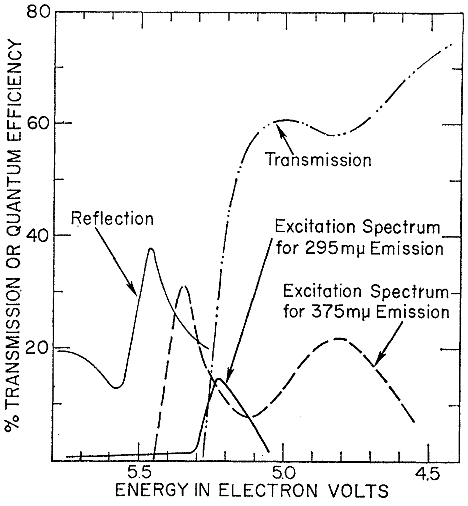

FIG. 7. Excitation and transmission spectra for an NaI crystal grown in Pt under an N_2 atmosphere with stoichiometric excess of I_2 diffused in at 500°C crystal temperature and approximately 1.4 atmospheres pressure of I_2. Measured at $-75°C$.

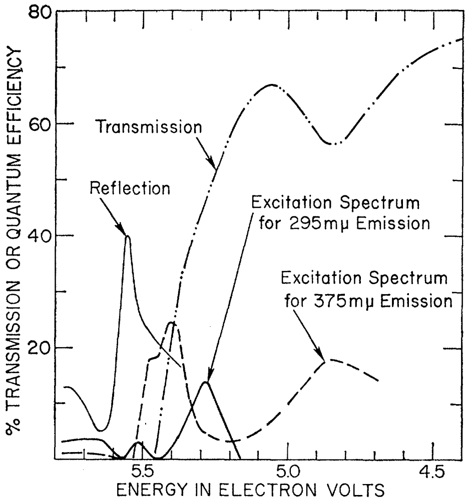

FIG. 8. Excitation and transmission spectra for an NaI crystal grown in Pt under an N_2 atmosphere with stoichiometric excess of I_2 diffused in at 500°C crystal temperature and approximately 1.4 atmospheres pressure of I_2. Measured at $-155°C$.

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[13] J. Rolfe, Phys. Rev. Letters **1**, 56 (1958).

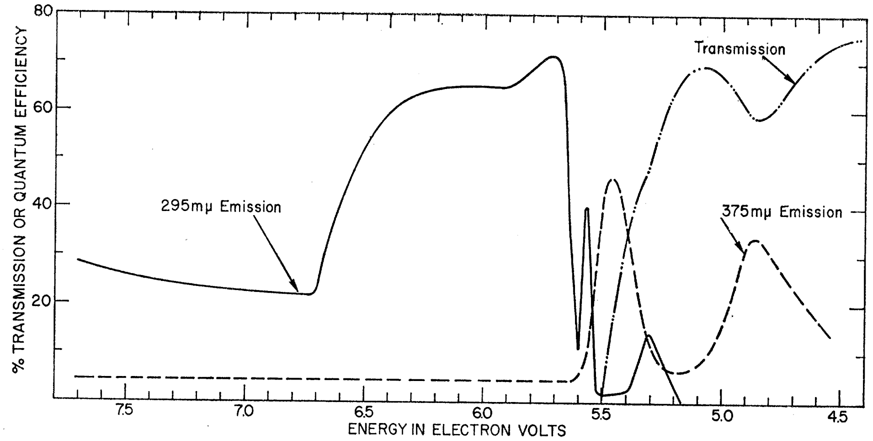

Fig. 9. Excitation and transmission spectra for an NaI crystal grown in Pt under an N_2 atmosphere with stoichiometric excess of I_2 diffused in at 500°C crystal temperature and approximately 1.4 atmospheres pressure of I_2. Measured at −190°C.

a vapor of NaOH did not exhibit an enhancement of the 5.3-ev excitation band.

325 mμ (*3.83* ev) *Emission Band*

The 325-mμ emission band appears only in the crystal doped with the highest concentration (0.1 mole %) of Tl (crystal *B*-2). This is coincidental with the absence in this one crystal of any 295-mμ emission. At first glance it might appear that the 325-mμ emission would simply be the residue to 295-mμ emission left after absorption by the principal absorption band at 4.26 ev due to Tl in the crystal. However, examination of Fig. 14 indicates that this is not the case. The excitation bands for the 325-mμ emission are found at 4.07 ev, 4.82 ev, and 5.05 ev. Additionally, this band has a small response to excitation in the 5.7-ev region. Two points should be noted with respect to the now hypothetical 295-mμ emission: first, its absence is not due to optical absorption exclusively, for there is a failure to overlap of approximately 40% of its area; and second, if there were actually an optical absorption and reemission taking place in the crystal, the 4.07-ev excitation band for the 325-mμ emission should be receiving a fair share, say 25% at least, so that the excitation spectrum for the 325-mμ emission should be at least 25% of that seen for the 425-mμ emission when excitation is in the 5.7-ev region.

The substantial strength of the 4.82-ev and 4.07-ev excitation bands seen in crystal *B*-2 as compared with their total absence in crystal *C*-1 (0.05 mole % Tl), indicates that these bands may arise from Tl ion pairs rather than single Tl ions because the Tl concentration ratios of these two crystals is only 2:1. However, an intensity of only $\frac{1}{2}$ of that observed for crystal *B*-2 would have been detected.

Each of the three excitation bands, giving rise to the 325-mμ emission lies approximately 0.1 ev on the low-energy side of three of the excitation bands for the 425-ev emission. It is interesting to compare the excitation bands for both the 325-mμ emission and the 425-mμ

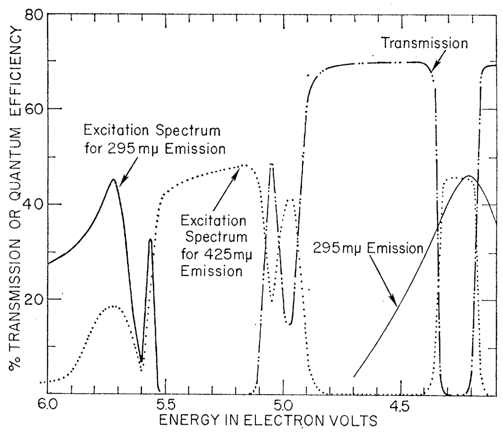

Fig. 10. Excitation and transmission spectra of an NaI crystal at −190°C containing 0.025 mole % Tl. The curve labeled 295-mμ emission was transposed from Fig. 2 and is shown here to indicate overlap with the absorption band due to Tl in the crystal.

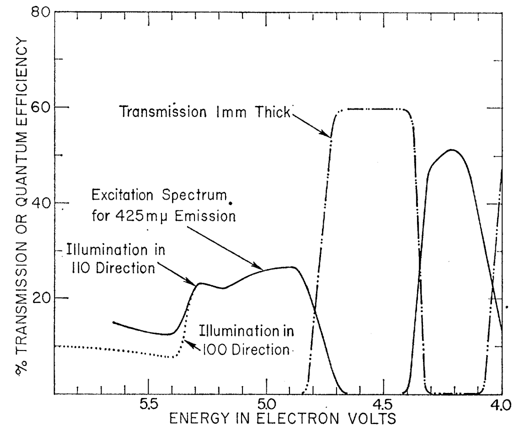

Fig. 11. Excitation and transmission spectra of an NaI crystal at +20°C containing 0.05 mole % Tl. For illuminating photon energies above 5.3 ev the quantum efficiency is greater for illumination at a 45° angle of incidence (solid curve) than for near normal illumination at a 5° angle of incidence (dotted curve). For illuminating photon energies below 5.3 ev the quantum efficiency was constant for any angle of incidence.

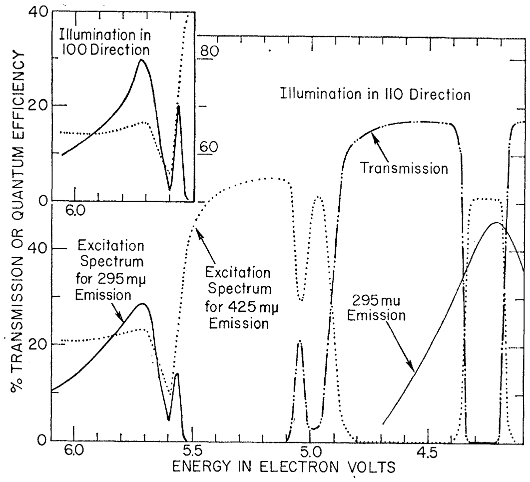

FIG. 12. Excitation and transmission spectra for an NaI crystal at −190°C containing 0.05 mole % Tl. The solid curves are for 295 mμ (4.20 ev) emission and the dotted curves are for 425 mμ (2.92 ev) emission. The main figure is for illumination at a 45° angle of incidence and the inset figure is for near normal illumination at a 5° angle of incidence. The curve labeled 295-mμ emission was transposed from Fig. 2 and is shown here to indicate overlap with the absorption band due to Tl in the crystal.

emission with the absorption bands observed in KI(Tl) by Yuster and Delbecq.[14] Applying an energy shift of +0.15 ev to the sodium iodide data, there is a remarkable correspondence. The three 425-mμ excitation bands correspond to bands in KI(Tl) at 4.40 ev, 5.08 ev, and at 5.32 ev which Yuster and Delbecq found to vary linearly with Tl concentration. Similarly, two of the 325-mμ excitation bands in NaI(Tl) correspond to doublet absorption bands in KI(Tl) at 4.92–4.96 ev and at 4.23-4.27 ev. Yuster and Delbecq found the strength of these latter bands varied approximately with the square of Tl concentration. No absorption band appears in the KI(Tl) results which could be taken to correspond to the 5.05-ev excitation band in NaI(Tl). No doubt such a band exists, but it is concealed by other much stronger bands.

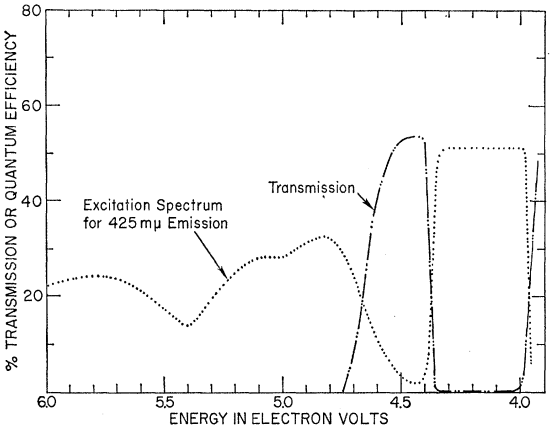

FIG. 13. Excitation and transmission spectra of an NaI crystal at +20°C containing 0.1 mole % Tl. Illumination was at an incidence angle of 45°.

375 mμ (*3.31* ev) *Emission Band*

This band is clearly associated with a stoichiometric excess of iodine, where it is strongest (Fig. 6–9). It is somewhat less strong in crystals grown in nitrogen, even weaker in the crystals grown in hydrogen (Fig. 4), and is absent in crystals doped with sodium (Fig. 5) or thallium (Figs. 10–14). It has two excitation bands: the lower energy one appears centered at 4.8 ev at 20°C and shifts to 4.85 ev at −190°C.

The second excitation band appears at 5.26 ev at 20°C and shifts monotonically to 5.47 ev at −190°C. It is interesting to note that the higher energy band maintains an almost constant energy difference of 0.1 ev with the reflection peak, which at the same time shifts from 5.36 ev to 5.59 ev. At +20°C the 375-mμ band is excited in the fundametal absorption region of energies above the first reflection peak. However, at lower temperatures the 375 mμ response to irradiation in this region dies out.

Since both excitation bands give rise to the same emission band, it is indicated that these two bands correspond to two excited states of the same center,

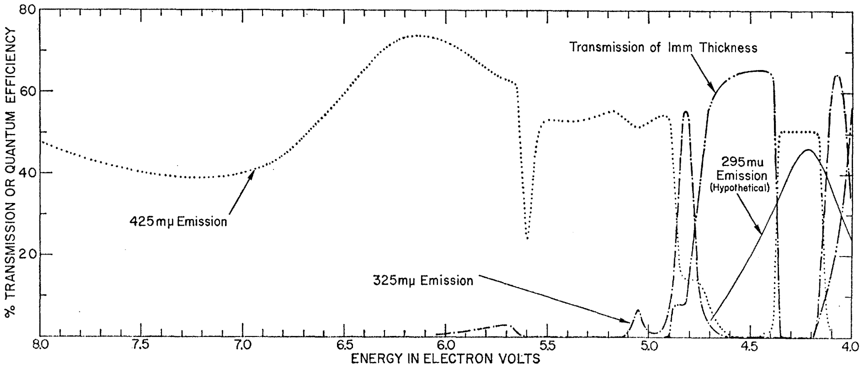

FIG. 14. Excitation and transmission spectra of an NaI crystal at −190°C containing 0.1 mole % Tl. Illumination was at an incidence angle of 45°. The curve labeled 295-mμ *emission* (*hypothetical*) was transposed from Fig. 2 and is shown here to indicate overlap with the absorption bands due to Tl in the crystal. Actually this crystal exhibited no 295-mμ emission. This is the only crystal exhibiting the 325 mμ (3.82 ev) emission band.

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[14] P. Yuster and C. Delbecq, J. Chem. Phys. **21**, 892 (1953).

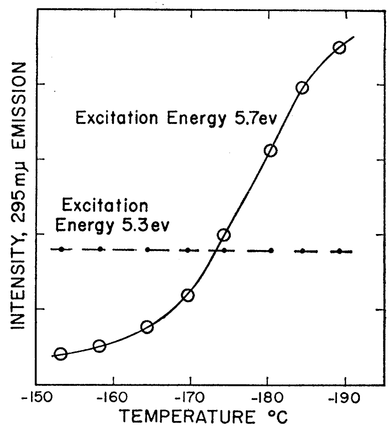

FIG. 15. Intensity, in arbitrary units, of the 295 mμ (4.20 ev) emission band versus temperature for excitation at 5.3 ev (dashed curve) and for excitation at 5.7 ev (solid curve). The data presented was for a crystal to which a stoichiometric excess of I_2 had been added. However, similar results were obtained for other samples as well. The results indicate that the excitation band at 5.3 ev is the principal one for the 295-mμ emission, and the higher energy excitation depends on a temperature-dependent energy transport mechanism.

rather than to two different types of center. The proximity of the higher energy excitation band to the first reflection peak and its nearly constant energy difference suggests that this band is an antimorph of the α or β band.

425 mμ (*2.92* ev) *Emission Band*

This emission band is the one normally associated with the scintillation light in thallium activated sodium iodide. The lowest energy excitation band for this emission is at 4.16 ev, +20°C and 4.26 ev at −190°C. Also at the lower temperature is a distinct band located at 4.97 ev and from 5.1 ev to the location of the first peak in the reflection spectrum there appears to be a continuum. The work of Yuster and Delbecq[14] on the absorption bands of potassium iodide indicates that in this region there are probably several overlapping bands. Figures 10, 12, and 14 illustrating the low temperature fluorescence, and absorption characteristics of these crystals, also show the emission spectrum for the 295-mμ band transposed from Fig. 2. It is interesting to note that this is in almost exact coincidence with the primary thallium absorption band. It would appear that the 425-mμ emission arising from illumination at energies above 5.6 ev could be accounted for by simple optical emission in the 295 mμ (4.20 ev) and partial reabsorption by the Tl band at 4.26 ev. In the case of crystal *A*-26 with a Tl concentration of 0.025 mole % (Fig. 10) this is apparently more or less the case, since the area overlaps for the 4.26-ev absorption band and the 295-mμ emission band is about the same as the ratio of intensities for excitation in the neighborhood of 5.7 ev. As should be expected, the shapes of the excitation spectra for the two emission bands in this region are similar. In the case of *C*-1 with twice the Tl concentration (Fig. 12), we see that the emission bands are now of comparable strength for excitation in the neighborhood of 5.7 ev, but they are no longer of similar shape. With higher Tl concentration still, crystal *B*-2, Fig. 14, the 295-mμ emission has vanished entirely, and the quantum efficiency of the 425-mμ emission for photon excitation energies higher than 5.7 ev is nearly constant and quite comparable with that found for direct illumination at 4.26 ev.

With excitation energies above 5.65 ev the shape of the excitation spectrum for 425-mμ emission in crystal *B*-2 at −190°C (Fig. 14) is very different from the shape of the excitation spectrum for the 295-mμ emission in crystal NaI (H_2) (Fig. 4). The foregoing seems to indicate that function of Tl in NaI crystals is more complex than that of a simple wavelength shifter which absorbs internally generated ultraviolet light in a band at 295 mμ and emits it at 425 mμ. It appears more likely that the Tl centers are capable of intercepting some form of internally migrating energy produced by illumination of the crystal at energies above 5.65 ev. The Tl centers seem to compete directly for the migrating energy with the centers producing the 295-mμ emission.

The NaI crystals containing Tl exhibit a preference for the 45° illuminating angle of incidence similar to that observed in crystals without Tl. This behavior is illustrated for crystal *C*-1 at +20°C in Fig. 11 and at −190°C in Fig. 12. However, while the 295-mμ emission exhibited nonisotropic characteristics the 425-mμ emission was found to be isotropic. The possible significance of the preferred illuminating angle of incidence is discussed below.

4. Energy Transport

This section consists of a qualitative discussion of the possible energy transport mechanisms involved in conveying energy from the crystal matrix itself to the more widely spaced luminescent centers.

In the energy range below 5.5 ev, the excitation bands for the various emission bands apparently correspond to various excited states of localized luminescence centers. In the energy range above 5.5 ev, incident photon energy can reach only a thin surface layer of the crystal penetrating a distance on the order of a few hundred angstroms or on the order of a hundred lattice unit distances. The probability that an incident photon would interact with one of the impurity or defect centers is negligible compared with its probability of interaction with the NaI crystal matrix itself. In examining the figures, it is apparent that in a number of instances a large fraction of the incident energy above 5.5 ev is ultimately emitted in the form of ultraviolet or visible light, in one of the four emission bands. All four of these emission bands seem to be identified with specific impurity or defect centers in the crystal; and the problem then remains: how is the energy transported from the crystal matrix to these luminescence centers? There appear to be three plausible mechanisms, photon emission and reabsorption, conduction electron and/or hole migration, and exciton migration.

In this discussion, photon emission and reabsorption is intended in mean luminescence in the crystal volume which is absorbed before escape, by luminescent centers which in turn emit lower energy photons.

Electron and hole migration implies the free, independent movement of electrons in the crystal's conduction band and of positively charged holes in the crystal's normally filled band. With an internal voltage applied, these charged particles should theoretically move in opposite direction making the crystal conductive.

Photon Emission and Reabsorption

Photon emission and reabsorption as the transport mechanism would imply that the pure crystal itself is luminescent when illuminated at energies above 5.5 ev. If this emission were in the optically clear region below 5.5 ev, certainly some of it would be directly detectable. Since none which could not be associated with a definite excitation band was detected, one must postulate emission in the opaque region, above 5.5-ev photon energy. If this were the case, the radiation would have to be reabsorbed and emitted a number of times before reaching the much less densely populated defect centers, but then energy loss due to crystal lattice relaxation would severely attenuate the observed photon efficiency. For this reason the possibility of photon emission and reabsorption apparently can contribute at best only a small fraction of the total energy transported.

Conduction Electron and Holes

Solid-state band theory predicts that the alkali halides should become photoconductive when illuminated with photons of energy about one ev greater than that found for the onset of fundamental optical absorption. The minimum energy for the onset of photoconduction, sometimes called the energy gap, is represented in band theory by a forbidden zone in which free electrons cannot exist.

Unfortunately, there is little experimental evidence to indicate what the energy gap is. Taylor and Hartman[15] recently made an extensive but fruitless search for internal photoconductivity in NaCl, KCl, KI, and LiF using photon energies ranging between 6 ev and 21 ev. Philip and Taft[16] has attributed the step seen in the absorption spectra of the alkali halides as corresponding to the onset of conduction. However, conduction was not actually observed. In NaI the step is at 5.8 ev. No positive experimental evidence for the value of the energy gap has appeared in the literature.

The second possibility for primary energy transport mechanism then is conduction electrons and/or holes. The possibility of producing luminescence in the thallium center by conduction electron capture has been discussed elsewhere.[8] It was pointed out that electron capture must also be accompanied by capture of a hole. The argument can be generalized in the following way: Assume a luminescent center based on a crystal defect or impurity. This center will have states analogous to that of a free atom, and in the absence of external excitation will be at its lowest or ground state. A conduction electron arriving at or passing close to this center can do one of two things. If it has sufficient energy, some of its energy may be passed on to the center, while the electron continues on its way at reduced energy. For this mechanism to occur the conduction electron would have to have a minimum energy of between 4.0 and 5.5 ev above the bottom of the conduction band since the excitation energies, which interest us here, lie in this energy range. However, in the present experiments none of the exciting photons had sufficient energy for this type of mechanism to occur. Alternatively, if the luminescent center produces a depression in the bottom of the conduction band, then an electron with any energy equal to or greater than the bottom of the conduction band could be trapped at the luminescent center. It is possible that luminescence emission could result from the capture of an electron only. Conversely, the same could be true of the capture of a hole only, since this would empty a lower state and permit an upper state to decay into it. However, with continuous exposure to exciting radiation, such luminescence would quickly die out because all centers would become saturated with either holes or electrons thereby terminating the luminescence. The description of continuous excitation and emission must be basically one of recombination, namely of electron and hole. However, it appears that the defect center is necessary to catalyze this recombination and that it is not capable of occurring in the perfect matrix.

These thoughts suggest that the energy transport mechanism involved in the observed luminescence may be an electron and hole which remain in close proximity, somehow associated, rather than wandering independently and making chance encounters with defect or impurity centers. In other words, it may be a kind of exciton, different from the one responsible for the peaks in absorption and reflection spectra.

Exciton Migration

There are three theoretical models which have been postulated to describe the exciton. One, used by von Hippel,[17] is called the electron transfer model, and assumes the transfer of an electron from a halide ion to a neighboring alkali ion. The second is called the excitation model and considers excited states analogous to the excited states of the free halide ion. Knox and

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[15] J. W. Taylor and P. L. Hartman, Phys. Rev. **113**, 1421 (1959).

[16] H. R. Philip and E. A. Taft, J. Phys. Chem. Solids **1**, 159 (1956); E. A. Taft and H. R. Philip, J. Phys. Chem. Solids **3**, 1 (1957).

[17] A. von Hippel, Z. Physik **101**, 680 (1936).

Inchauspé[18] have recently shown that either of these models can be used to predict rather well the exciton peaks in the absorption bands of alkali halides. The third model, used by Wannier,[19] considers excited states analogous to those of a free hydrogen atom. This third case starts from the basis of the periodic potential of a polar crystal and assumes that the electron and hole are bound together by electrostatic force. When quantized the theory produces a multiplicity of energy levels. This last model fails completely to predict the peaks in the alkali halide absorption bands. It is beyond the scope of this article to attempt a rigorous theoretical treatment, but the Wannier model appears to be a perfectly good one and it is a severe temptation to suggest at this point that it may be applicable and may properly describe the underlying continuum of the fundamental absorption in alkali halides.

Migration of the excitation or electron transfer type of exciton as a primary means of energy transport for 295-mμ emission can apparently be rejected. All figures illustrating the excitation spectra show a deep dip at the energy of the first absorption or reflection peak, much deeper than the increase in reflectivity at this region could alone account for (Fig. 3). In the region of the first absorption peak little energy is transported to a luminescent center to appear as ultraviolet or visible light. (Teegarden[3,20] observed a similar effect in the excitation spectrum of KI.) Furthermore, at the location of the second absorption or reflection peak, we find a dip in the excitation spectrum of the thallium free crystals.

The explanation of the observed characteristics of the 295-mμ excitation spectra would be considerably facilitated by acceptance of the Wannier exciton model. First, as is suggested above, one must assume that the phenomenon is basically one of recombination, with a defect or impurity center acting as a catalyst. The rapid decay[7,8,21] of the 295-mμ luminescence coupled with its constant quantum efficiency for varying incident photon flux densities at the lower energy end of the excitation continuum suggests that the recombining electron and hole must be in close proximity, and somehow associated, rather than wandering aimlessly and making chance encounters.

Furthermore, some explanation is required for the observed directionality of the emitted luminescence, when the exciting energy is 5.7 ev or above. The fact that a momentum vector seems to be preserved from incidence of the illuminating photon, through energy transport capture, decay, and emission requires that the transport mechanism be capable of a vector characteristic. The independent wandering of an electron and hole cannot be described with a vector, but if these two are bound in an excited state they can be described by, for example, the angular momentum vector or velocity vector of a kind of exciton.

Finally, it was also observed that there was a preference for incident radiation in 110 direction over the 100 direction (Figs. 4, 11, 12). It is immediately obvious that the periodic potential of a polar crystal looks entirely different when viewed in the 110 direction from that in the 100 direction. Possibly the Wannier exciton propagates most readily in the 110 direction.

IV. CONCLUSIONS

The reflection spectrum of NaI single crystals is qualitatively very similar to the published absorption spectra of NaI evaporated films. One feature of the reflection spectrum, not seen in the absorption spectra, is an inflection appearing at 5.62 ev on the high-energy side of the lowest energy absorption or reflection peak.

Four prominent fluorescence emission bands were investigated. One at 295 mμ (4.20 ev) seems to be characteristic of pure NaI since it was its strongest in the purest crystals which we produced and was eliminated only in a crystal containing 0.1 mole % Tl. Still, the fact that it has an excitation band whose energy is less than that of the fundamental absorption edge, indicates that this luminescence depends on some kind of center, rather than the direct decay of excitons as has been suggested.[8] The nature of the center was not determined, but since other possibilities have been eliminated to some extent, it may simply be a dislocation.

The 375 mμ (3.31 ev) emission band was clearly identified with a stoichiometric excess of iodine in the crystal. This emission was produced by illumination in either of two excitation bands indicating two excited states of a single type of center, possibly a *V* center.

The 425 mμ (2.92 ev) and the 325 mμ (3.82 ev) emission bands are clearly identified with Tl centers. The former seems to be single Tl ions in the NaI lattice, and the latter seems to be Tl ions that are nearest neighbors. Three distinct excitation bands were identified for each of these emission bands. The three excitation bands for the 325-mμ emission lie approximately 0.1 ev on the low-energy side of the three excitation bands for the 425-mμ emission.

With illumination of the crystal by ultraviolet light of energy greater than that corresponding to the fundamental absorption edge, where the photon energy is absorbed primarily by the NaI matrix rather than defect or impurity centers, some mechanism is required for the transport of energy from the point of absorption to the luminescent centers. The results of the experimental investigations provide some evidence that an important contributor to the energy transport is a mobile exciton of the Wannier type. On the other hand, the exciton models which have been used successfully in calculating the locations of peaks in alkali halide absorption spectra evidently do not contribute to the energy transport. It appears that the name exciton is currently applied to two distinct phenomena. Since the Wannier exciton

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[18] R. S. Knox and N. Inchauspé, Phys. Rev. **116**, 1093 (1959).

[19] G. H. Wannier, Phys. Rev. **52**, 191 (1937).

[20] K. J. Teegarden, Phys. Rev. **105**, 1222 (1957).

[21] W. Van Sciver and L. Bogart, IRE Trans on Nuclear Sci. **NS-5**, 90 (1958).

apparently exists and is mobile, it would seem that it is the proper exciton. Conversely, the energy absorbed in the peaks of the alkali halide absorption spectra is apparently not mobile. Perhaps these should be called excitation peaks rather than exciton peaks.

V. ACKNOWLEDGMENTS

It is with the greatest pleasure that I acknowledge the assistance of Professor Robert Hofstadter, who stimulated my original interest in this subject, who has been a source of constant encouragement, and who read the rough manuscript of this article and made valuable clarifying suggestions to improve the final draft of it. Thanks also go to Dr. Werner Martienssen for suggesting the reflection measurements, and to Hellmut Gründig, for providing me with a copy of his unpublished work on KBr involving removal of hydroxide and zone refining.

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Optical Measurement of the Plasma Frequency and $M_{2,3}$ Band of Chromium

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(Received July 7, 1960)

The transmission of thin chromium films has been measured in the extreme vacuum ultraviolet. The onset of transmission at 500 angstroms or 24.8 electron volts agrees well with the theoretical prediction by Pines of 25 electron volts; it also agrees well with the experimental electron eigenlosses measured by Watanabe, and Marton and Leder, of 26 electron volts and 22 electron volts, respectively. The $M_{2,3}$ band was also measured.

I. INTRODUCTION

THE free-election theory[1–3] has proven successful in the understanding of many of the important properties of metals. On this model, the electrons in a metal may be considered to be free, and to move in a smoothed out potential of the ion cores and the other free electrons. On this model, the electrons move independently of one another; this will be called the independent-particle free-electron model. It is to be noted that if the Pauli Exclusion Principle is taken into account, the particles do not move completely independently of one another; electrons with the same spin tend to keep away from one another.

However, the independent-particle free-electron picture can be used successfully to calculate some of the optical properties of a metal.[3] In particular, a calculation using classical electromagnetic theory, and the assumption of a free electron with damping acted upon by a periodic electric field, will yield values for a complex dielectric constant which are consistent with experiment. For a system with no damping, the dielectric constant should be imaginary at wavelengths greater than the critical wavelength, and real for wavelengths shorter than the critical wavelength. By use of the Fresnel equations, and the fact that the imaginary part of the dielectric constant is proportional to the linear absorption coefficient, it can be seen that this is equivalent to stating that as the energy increases, the metal goes from a reflecting to a transmitting region. Hence, a measurement of the transmission should yield the critical wavelength; this depends upon the electron density and the effective mass. Friedel[4] has mentioned that the real electron mass should be used at the high frequencies which correspond to the ultraviolet. Kittel[5] has compared the results of optical measurements on the alkali metals, and it appears that use of the real mass yields better results than use of an effective mass.

An alternative explanation of this phenomenon can be made on the basis of the collective-interaction free-electron model.[6,7] In this model, the long-range Coulomb interaction among all of the electrons is taken into account. Hence, instead of each electron being unaware of the individual presence of every other electron, the motion of one electron affects the motion of every other electron in the system. This results in a collective mode of behavior of the system in which the correlated motion corresponds to collective oscillations of the system as a whole, which resemble the plasma oscillations in gaseous discharge. This occurs for distances large compared to the interatomic spacing. An interesting point is that this more complete treatment also shows that the in-

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[*] Now at National Aeronautics and Space Administration, Goddard Space Flight Center, Washington, D. C.

[1] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. IV, XVII.

[2] N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Dover Publications, New York, 1958).

[3] M. Parker Givens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 6, p. 313.

[4] J. Friedel, Notes for École d'Été sur l'Etat Solide, Paris, 1958 (unpublished), p. 29.

[5] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1953), 2nd. ed., p. 266.

[6] S. Raimes, in *Reports on Progress in Physics* (The Physical Society, London, 1957), Vol. 20, p. 1.

[7] D. Pines, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 367.