material, as a function of ionization density and Tl content. Unfortunately, this is not possible in NaI(Tl) or CsI(Tl), as a consequence of the overlap between the ultraviolet band and the Tl absorption. This overlap does not occur in KI(Tl), however, so that the crystals of KI(Tl) would provide a favorable medium for such a study.

Scintillation Process in CsI(Tl). II. Emission Spectra and the Possible Role of Self-Trapped Holes*

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The luminescence emission spectra of CsI(Tl) crystals containing varying amounts of Tl have been measured upon excitation by gamma rays, protons, and alphas. The principal features include a broad Tl emission band centered near 5500 Å and a narrower band centered near 3300 Å which is characteristic of the host crystal. This 3300-Å band is analogous to near-ultraviolet emission bands observed in NaI and KI. It is found for CsI(Tl) that the intensity of the 3300-Å band relative to the Tl band is greatest upon excitation by radiation of high dE/dx. It is suggested that the 3300-Å band arises from the recombination of free electrons with self-trapped holes. Evidence from other investigations supporting this hypothesis is summarized.

I. INTRODUCTION

IN connection with the experimental program described in Part I,[1] it was necessary to measure the emission spectra of the various CsI(Tl) crystals used upon excitation by radiations of considerably different stopping power. The results of these measurements are of some intrinsic interest, and for this reason are presented here. These measurements do not constitute the first studies of the emission spectrum of CsI(Tl) crystals. In fact, several authors[2-5] have previously reported the emission spectrum, with results which are not in complete agreement. The present measurements, however, are unique in that they present a systematic study of the spectra upon changing both the Tl content and the average stopping power of the exciting particle.

II. EXPERIMENTAL METHOD AND RESULTS

Emission spectra were measured with a Bausch and Lomb 500-mm focal length grating monochromator which had a nominal dispersion of 33 Å per mm. Light from the exit slit of the monochromator was detected with an RCA-7265 photomultiplier. The relative spectral response of the monochromator-photomultiplier system was measured with a tungsten-filament lamp whose emission spectrum was known from a previous calibration at the National Bureau of Standards. Emission spectra were measured upon excitation by 50- and 250-keV x rays, 1.4- and 4.4-MeV protons, and 2.0- and 8.7-MeV alpha particles. The x-ray beam was filtered[6] to provide a reasonably limited band of x-ray energies: The lower energy beam extended from about 30 to 50 keV, and the higher energy beam extended from 150 to 275 keV. Monoenergetic protons and alphas used for excitation were obtained with the 5.5-MV Van de Graaff generator. The current density of both protons and alphas on the crystal surface was limited to a maximum value of 10^{-9} A/cm². The total light output of the crystal was continuously monitored to account for fluctuations in beam current.

Results of the spectral measurements are summarized in Figs. 1 through 3, in which the ordinate has been

* This work was included in a thesis submitted by R. Gwin in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Tennessee.

† Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

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[2] H. Knoepfel, E. Loepfe, and P. Stoll, Helv. Phys. Acta 30, 521 (1957).

[3] G. Hrehuss, Nucl. Instr. Methods 8, 344 (1960).

[4] R. G. Lagu and B. V. Thosar, Proc. Indian Acad. Sci. A53, 219 (1961).

[5] Z. L. Morgenshtern, Opt. i Spektroskopiya 8, 672 (1960); 7, 231 (1959) [translations: Opt. Spectry. (USSR) 8, 355 (1960); 7, 146 (1959)].

[6] J. C. Villforth, R. D. Birkhoff, and H. H. Hubbell, Jr., Oak Ridge National Laboratory Report ORNL-2529, 1958 (unpublished).

corrected for the spectral response of the mono-chromator-photomultiplier system. In the figures all curves are normalized to the same area, hence, the same total number of emitted photons. Figure 1 presents spectra obtained from the various radiations on one crystal of CsI(Tl) of Tl content 0.002 mole %; Fig. 2 presents similar data for 0.046 mole % Tl. Figure 3 shows spectra obtained from crystals of varying Tl content, all excited by 4.4-MeV protons. The pertinent features to be noted in these spectra are the broad band centered near 5500 Å (for crystals containing Tl) and the weak band centered near 3300 Å whose relative intensity is a sensitive function of the exciting radiation. In particular (see Fig. 1), the intensity of the 3300-Å band relative to the total emission intensity is a mono-tonically increasing function of the average ionization density of the exciting particle. (The average ionization density increases in the order of presentation of the legend in Fig. 1.)

The origins of both the 3300- and 5500-Å emission bands have been studied by previous investigators. In


FIG. 1. Emission spectra of a CsI(Tl) crystal having a Tl content of 0.002 mole %, upon excitation by various radiations. Curves for 250-keV x rays, 1.4-MeV protons, and 8.7-MeV alpha particles are indistinguishable above 4000 Å.
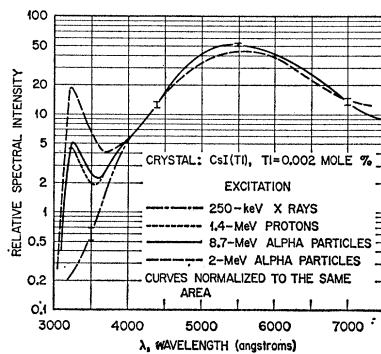
all studies it is found that in crystals containing Tl the emission spectrum is dominated by the broad yellow band. This band is thus associated with emission from Tl luminescence centers, and is referred to as the Tl band. Studies of CsI crystals in which no Tl is added, especially the work of Morgenshtern,[5] reveal that the emission spectrum is composed of two bands, an ultra-violet band (centered near 3300 Å) and a blue band whose exact spectral position may vary from one crystal to another. For a given excitation intensity, these bands, characteristic of the nonactivated crystal, are much stronger at liquid-nitrogen temperature than at room temperature. On the basis of his experiments Morgenshtern concluded that the ultraviolet band is a property of the perfect crystal and is not associated with impurities or imperfections, whereas the blue band was tentatively associated with the presence of vacancies. This interpretation of the origin of the ultra-violet band is reinforced by later investigations of excitation spectra.[7] Further, recent experiments by

FIG. 2. Emission spectra of a CsI(Tl) crystal having a Tl content of 0.046 mole %, upon excitation by various radiations.
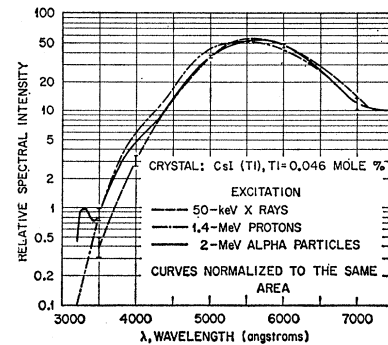
Besson and co-workers[8] led to the same conclusion regarding the ultraviolet band, and to the interpretation of the blue band as originating from cation vacancies in equilibrium with divalent impurities, e.g., Ca, Fe, or Mg. It may be further noted that ultraviolet emission bands have been observed in[9] KI at ~3300 Å and in[10] NaI at ~3000 Å. In both KI and NaI these emission bands are excited by the absorption of light in the fundamental band region, and thus appear to be analo-gous to the 3300-Å band of CsI. This analogy has been discussed by Vasil'eva and Morgenshtern.[7]

The present spectral measurements lead to two significant observations: (1) For a given Tl content the relative intensity of the 3300-Å band increases with an increase in ionization density of the exciting radiation; and (2) For a given exciting particle the relative intensity of the 3300-Å band increases as the Tl content is decreased. Effects analogous to both items (1) and (2) have been observed in NaI(Tl).[11] It, thus, appears from these two observations that the luminescence centers responsible for the 3300-Å band compete with
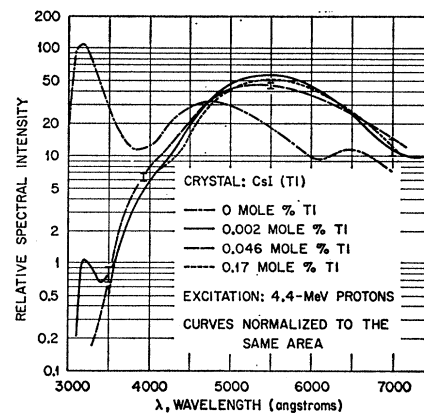

FIG. 3. Emission spectra of CsI(Tl) crystals having various Tl contents for excitation by 4.4-MeV protons.

[7] N. N. Vasil'eva and Z. L. Morgenshtern, Opt. i Spektroskopiya 12, 86 (1962) [translation: Opt. Spectry. (USSR) 12, 41 (1962)].

[8] H. Besson, D. Chauvy, and J. Rossel, Helv. Phys. Acta 35, 211 (1962).

[9] K. Teegarden and R. Weeks, J. Phys. Chem. Solids 10, 211 (1959).

[10] W. J. Van Sciver, Phys. Rev. 120, 1193 (1960).

[11] W. J. Van Sciver, IRE Trans. Nucl. Sci. 3, 39 (1956). Also, Stanford University Report HEPL 83, 1955 (unpublished).

Tl sites for the capture of energy carriers resulting from the primary excitation, and that this competition is a function both of ionization density and Tl concentration.

The emission spectrum of nonactivated CsI, Fig. 3, is dominated by the 3300-Å band and contains in addition a broad band centered near 4700 Å and a weak band at about 6500 Å (which may be due to second-order reflection from the 3300-Å band). The 4700-Å band is presumably analogous to the blue band described above and is to be associated with crystalline imperfections.

It may be noted that the 3300-Å band characteristic of the host crystal overlaps an absorption band of CsI(Tl) which is due to the presence of Tl.[12] Thus, light emitted in the 3300-Å band will be partially absorbed in a crystal containing Tl, and is in fact capable of exciting emission in the yellow Tl band.[2,5] For this reason, the measured emission spectra are somewhat distorted from the true primary emission spectra; the primary emission spectra will contain more light in the 3300-Å band and less in the Tl band. An analogous situation is found in NaI(Tl).[10] Measurements of the transmission of light in the region of 3300 Å by the 0.2-cm-thick CsI(Tl) crystal of 0.002 mole % Tl showed that about 50% of the incident light was absorbed.[13] For a crystal of similar thickness containing 0.17 mole % Tl, the fraction of incident light at 3300 Å which was transmitted was less than 1%. The absorption process is, thus, a significant effect and may lead to a considerable distortion of the primary emission spectrum. It is estimated that the intensity of the 3300-Å band from alpha excitation, in Fig. 2, is a factor of 10 reduced from its initial intensity in the primary spectrum. It must be recognized that the existence of this mechanism for stimulating Tl emission introduces a complication in the quantitative interpretation of Tl emission intensity as a function of ionization density or Tl concentration: Clearly, the Tl band can be excited directly by the capture of energy carriers, or by excitation from the 3300-Å band.

Finally, it may be noted that the dependence of emission spectra on ionization density observed in the present work does not agree with the measurements of Hrehuss.[3] This difference may arise in part from the intensity of the exciting radiation: The current density in the present experiments was a factor of 10³ less than that used by Hrehuss.

III. DISCUSSION

It was indicated in Part I[1] that the results of the experiments described therein argue against any significant saturation of the Tl centers upon excitation by a highly ionizing particle. The increase in relative intensity of the 3300-Å band with ionization density is thus apparently not simply a case of "forcing" energy carriers to these centers as the Tl sites are occupied. The alternative interpretation is that the centers responsible for the 3300-Å band are created by the exciting radiation, and that the number of these centers created per unit path length of the primary particle is an increasing function of ionization density. In the following discussion the ultraviolet emission bands of CsI, KI, and NaI are considered to be analogous and will be discussed as arising from the same mechanism. It is here suggested that this mechanism may be the recombination of free electrons with self-trapped holes. We specify the hole-trapping mechanism as that of the *self*-trapped hole, rather than trapping at some point defect created by the primary particle, on the basis of energy considerations. The energy-conversion efficiency for the scintillation process in nonactivated alkali iodides at low temperatures is such that one photon is emitted for an energy loss of only 10–20 eV by the primary particle. This fact eliminates the possibility that the luminescent center is a defect associated with a vacancy that is created by the incident particle, as the energy consumed in such a process would lead to a scintillation efficiency orders of magnitude lower than that observed. For example, Rabin and Klick[14] have found experimentally in various alkali halides that the energy required to create an F center at low temperatures, presumably by first creating the halide-ion vacancy, amounts to 10³ to 10⁵ eV. The energy required to displace an anion from its lattice site following multiple ionization has been calculated for several alkali halides by Varley,[15] and is found to be in reasonable agreement with the experimental values of 10³ to 10⁵ eV.

The existence at low temperatures of stable halide molecule ions of the type X_2^- (or self-trapped holes) has been confirmed in various alkali halides by studies of optical absorption spectra and electron paramagnetic resonance (EPR) spectra.[16] These centers are observed after x-ray irradiation at liquid nitrogen temperature. The rate of formation of X_2^- centers is increased orders of magnitude by the addition of an impurity such as Tl⁺ to the crystal. This effect is attributed to the very high electron capture cross section of the Tl⁺ ion. The lifetime of X_2^- molecule ions is a function of temperature; at a sufficiently low temperature (typically liquid nitrogen) the centers are stable for an indefinite period. As the temperature is raised the ions are capable first of reorientation among the equivalent ⟨110⟩ directions (in a face-centered cubic lattice, as KI) and, at a somewhat higher temperature, the ions (or self-trapped holes) are apparently capable of moving through the lattice and being annihilated at a Tl⁰ center with the emission of luminescence radiation characteristic of the

[12] M. Forro, Z. Physik **58**, 613 (1929).

[13] These transmission measurements were performed by D. A. Costanzo of this Laboratory.

[14] H. Rabin and C. C. Klick, Phys. Rev. **117**, 1005 (1960).

[15] J. H. O. Varley, J. Phys. Chem. Solids **23**, 985 (1962).

[16] See, for example, C. J. Delbecq, W. Hayes, and P. H. Yuster, Phys. Rev. **121**, 1043 (1961), and references therein.

Tl+ ion.[17] In KCl, for example, the peak in the glow curve attributed to the above process occurs at about $-65°C$. In KI a glow curve peak, attributed to the release of trapped holes,[9] occurs at $-155°C$.

CsI has the body-centered cubic structure of CsCl. A recent EPR study of irradiated[18] CsCl has shown the existence of a "hole"-type center which is tentatively identified as the Cl_2^- center. It, thus, appears that self-trapped holes can exist in the body-centered cubic structure as well as the face-centered cubic.

With regard to the scintillation process, the suggested role of self-trapped holes appears to be qualitatively consistent with experiment. On the basis of this mechanism, the primary charged particle creates, per unit path length, a number of electrons and holes proportional to its ionization density; the holes may then be self-trapped with a lifetime in the trapped state which is a function of temperature. Free electrons may be captured at Tl+ sites, or may recombine directly with a trapped hole resulting in the emission of a 3300-Å photon. The probability that a given electron will recombine with a trapped hole rather than suffer capture at a Tl+ site will be an increasing function of the density of trapped holes, hence, an increasing function of ionization density. Thus, the relative intensity of the 3300-Å band is expected to increase with ionization density, in accord with experiment. Further, this concept treats luminescence from the Tl+ center as arising from a process in which the Tl+ first captures an electron. A hole which is initially self-trapped can be thermally excited to the valence band and can migrate to the Tl⁰ center in a time which is characteristic of the temperature and depth of the hole trap. Capture of the hole at the Tl⁰ center completes the cycle and permits luminescence radiation characteristic of the Tl+ center. This process is identically the same as that indicated by Delbecq et al.[17] in the case of KCl doped with Tl+, Ag+, or Pb++. This description of the scintillation process clearly requires that the hole be alternately localized (to permit electron capture) and mobile (to permit migration to a Tl⁰ center). This description, thus, implicitly assumes that hole migration occurs by thermal excitation to the valence band followed by retrapping to the localized self-trapped state or trapping at an impurity center and final annihilation at a Tl⁰ site. For a crystal containing Tl+ it is thus expected that the Tl+ luminescence must decrease at sufficiently low temperatures as the probability of thermal excitation of a hole will be small. This is, in fact, found to be the case in several Tl-activated alkali halides.[19]

For irradiation of the crystal by gamma rays, then, the main process of exciting Tl luminescence would be by the successive capture of an electron and a hole. For a particle of high dE/dx, for which there is relatively more light in the ultraviolet band, Tl luminescence may be stimulated by optical absorption or by sensitized luminescence in those crystals for which the Tl absorption spectrum overlaps the ultraviolet emission band. The possibility of exciting the Tl center by capture of an exciton is not excluded.

Emission of the ultraviolet band at a high temperature (such as room temperature) on the basis of the present model may be questioned as it is known from optical and EPR experiments that I_2^- ions are unstable at room temperature. "Unstable" in this instance means that the lifetime of the hole in the trapped state is short compared to the duration of an experiment. For the described radiative process to take place it is required only that the lifetime in the trapped state be comparable with the time required for electron capture and emission.

The role of self-trapped holes as suggested above appears further to be consistent with several experimental observations in both KI and NaI. In the case of KI, Teegarden and Weeks[9] have studied extensively the 3700-Å emission band in nonactivated crystals and conclude that this emission results from the recombination of electrons with trapped holes (though not necessarily self-trapped). They further attribute a red luminescence, observed upon warming the previously irradiated crystals, to the thermal excitation of trapped holes followed by recombination with electrons at unspecified sites; the maximum in the glow curve of this luminescence occurred at $-155°C$. They further observed that the relative quantum yield of the 3700-Å band, for excitation in the F band of a previously irradiated crystal, decreased rapidly for temperatures above $-173°C$. This corresponds quite closely to the temperature $(-180°C)$ at which the disorientation rate of I_2^- ions in KI was observed to be a maximum.[16]

Studies of thermoluminescence in NaI(Tl)[11] have revealed effects exactly analogous to observations of thermoluminescence resulting from the release of self-trapped holes in KCl[17] activated with Tl+, Ag+, or Pb++. In KCl it was observed that the thermoluminescence emission spectrum was a property of the impurity ion. In NaI(Tl) it was found that the thermoluminescence spectrum corresponded to the emission spectrum of the Tl ion. The ultraviolet emission band (~3000 Å) characteristic of pure NaI was not observed in thermoluminescence. It was further observed in NaI(Tl) that the intensity of the thermoluminescence emission per unit energy deposited in the crystal was greater for gamma-ray excitation than for alpha excitation. This fact is consistent with the present interpretation, since an electron released upon gamma-ray excitation will have a greater probability of capture at a Tl+ site than an electron released upon alpha excitation.

Another aspect of the ultraviolet emission band of NaI appears to be consistent with the present interpretation. Measurements of the luminescence yield of this

[17] C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. 111, 1235 (1958).
[18] F. Hughes and J. G. Allard, Phys. Rev. 125, 173 (1962).
[19] W. W. Managan, IRE Trans. Nucl. Sci. 9, 1 (1962).

band[10] upon excitation by ultraviolet showed that the quantum efficiency *increased* as the incident photon flux increased for excitation by 7.7-eV photons. For excitation with photons having an energy of 5.7 eV the quantum efficiency was independent of the incident photon intensity. It is noted that 5.7 eV is just less than the band gap of NaI (5.8 eV)[20] while a 7.7-eV photon is capable of producing ionizing events. As the excitation intensity with 7.7-eV photons increases, the steady-state density of I_2^- ions increases while the density of other electron traps (associated with impurities or imperfections) remains constant. On the basis of the present interpretation this situation would lead to an increase in the quantum efficiency of the ultraviolet band as the excitation intensity increases, in accord

with experiment. The fact that the ultraviolet emission band is stimulated by light in the fundamental band region (5.7 eV and below in NaI) indicates that the ultraviolet band may result from the radiative decay of an exciton, as previously suggested by Van Sciver.[11] This implies that the excited state of both the $(I_2^- + e)$ center and the exciton decay radiatively with the same emission spectrum. The interpretation suggested in this paper is, therefore, similar to that previously given by Van Sciver[11] with regard to the emitting excited state.

ACKNOWLEDGMENTS

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Helicons and Magnons in Magnetically Ordered Conductors

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The character of magnons and helicons in magnetically ordered conductors is considered. Conductors become transparent to circularly polarized electromagnetic waves, helicons, when $\omega_c\tau\gg1$, where ω_c is the cyclotron frequency and τ is the relaxation time of the conduction electrons. It is shown that, in general, there exists a strong coupling between helicons and magnons, so strong that a perturbative approach is not adequate. The effect of this strong coupling is calculated and is shown to produce large effects on the magnon and helicon spectra at long wavelengths. The coupling between magnons and helicons can be varied by changing the external magnetic field. These effects should be experimentally observable.

W E consider the problem of the existence of helicons in magnetically ordered conductors, and their interaction with spin waves. A helicon, called a whistler in atmospheric physics, is a mode of propagation of a circularly polarized electromagnetic wave through a charged plasma in a magnetic field. Recently, helicons have been observed in very pure metals at liquid-helium temperatures[1–3] where they have also been called magnetoplasma oscillations. In the limit approached in these experiments of $\omega_c\tau\gg1$, where ω_c is the cyclotron

frequency of the electrons in the magnetic field and τ is their relaxation time, the electron plasma is transparent to one sense of circularly polarized radiation, the one that rotates in the same direction as the electrons around the magnetic field, while it is reflecting to the other sense. The angular frequency, ω, of the helicons of wave number q is given by the usual relation for electromagnetic waves

$$\omega^2 = (c^2/\mu\epsilon)q^2, \qquad (1)$$

where μ and ϵ are the magnetic permeability and dielectric constants, respectively. For nonmagnetic metals and for frequencies near zero[2]

$$\epsilon = 4\pi nec/\omega B, \qquad (2)$$

and to a good approximation $\mu = 1$. Here B is the magnetic induction and there are n effective conduction

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[3] P. Cotti, P. Wyder, and A. Quattropani, Phys. Letters **1**, 50 (1962).