INTRODUCTION

A single crystal of CsI (Tl) supplied by Harshaw Chemical Co., was studied at room temperature for its luminescence spectra under ultra-violet excitation and scintillation spectra under γ-rays. As pointed out by Sciver W. J. Van, the identity of luminescence centres in the two types of excitation cannot be assumed unless it is established that the emission spectrum in fluorescence under ultra-violet and that in scintillation under γ-rays are the same. There does not seem to be any systematic spectroscopic study of the scintillations excited by γ-rays in Thallium-activated alkali halide crystals, though these crystals are now in constant use for γ-ray scintillation spectrometry. The purpose of these studies was to compare the emission spectra of CsI (Tl) crystal under ultra-violet and γ-ray excitations. If the emission spectrum of scintillations under γ-rays had more than one band, it would be of great interest to determine the decay time and decay characteristics of each of the emission peaks separately. For this reason, it is necessary to measure the emission spectrum of scintillations in some detail. For purposes of comparison, the emission spectra of Thallium-activated CsBr, NaI and KI were also studied.

EXPERIMENTAL ARRANGEMENT

A Steinheil 3-prism spectrograph with collimator and camera having apertures ∼f/3 and ∼f/4 respectively was employed and the spectra in the visible range 4000 Å–6000 Å were photographed on a Kodak Tri-X film. The average reciprocal dispersion of the spectrograph in the visible range was ∼50 Å/mm. A condenser with an aperture ∼f/1.5 collected light from the crystal on to the slit of the spectrograph. As the spectra at room temperature were expected to be broad continua and the light output was very low especially with γ-excitation, the slit-width was kept as large as 400 μ. Co⁶⁰ ( ∼7 m.c.) provided a γ-ray source while suitable filter solutions were employed to cut off visible radiation and transmit mainly ultra-violet from an intense high-pressure quartz mercury lamp. The crystal
was kept in a light-tight housing as exposures of the order of a few days were necessary to obtain spectra under \(\gamma\)-ray excitation.

The liquid filters used with the ultra-violet source were as follows:

1. \((\text{CoSO}_4 + \text{NiSO}_4)\) solution in water in a quartz cell having a path-length of approximately 2 cm. transmits the radiation between 3600 Å and 2300 Å with a peak transmission of \(\sim 75\%\) at 3000 Å. This filter could thus entirely remove the visible continuum in the spectrum of Hg-source and reduce considerably the intensities of lines in the visible region. This was necessary to prevent visible light reflected and scattered from the crystal, masking the genuine luminescence spectrum.

2. \((\text{I}_2 + \text{CCl}_4)\) in a similar quartz cell transmits between 4400 Å and 3000 Å with a peak transmission of \(\sim 60\%\) at 3800 Å.

These filters were employed one at a time between the Hg-source and the crystal. With them, the space in the visible range was made clear, as it were, for the true luminescence spectrum to appear. Duration of exposures required were of the order of a few minutes.

**Results**

The spectrograms thus obtained were microphotometered on a Hilger non-recording instrument. The results are given in Fig. 1(a)-1 (g).

The scintillation spectrum of CsI(Tl) excited by \(\gamma\)-rays is continuous between 4000 Å and 6000 Å with at least three peaks at approximately 5950±50 Å, 5700±50 Å and 4750±50 Å. The three peaks are very well pronounced. There is probably a fourth peak at 4400 Å but this is rather doubtful since it appears as a small shoulder to 4750 Å band [Fig. 1(a)]. The luminescence spectrum of CsI (Tl) is described as ‘white’ by J. B. Birks while the range is given by Hahn and Rossel as 4200–5700 Å.

When fluorescence is excited by ultra-violet light with a continuous range between 2300 Å and 3600 Å, the emission spectrum is continuous with peaks at identical wavelengths as in scintillation spectrum. These peaks, however, are not as well resolved as in \(\gamma\)-ray excitation experiment [Fig. 1(b)]. With the exciting spectrum comprising of wavelengths between 3000 Å and 4400 Å, only a part of the emission spectrum appears, i.e., only the wavelengths greater than 5600 Å are excited. Nevertheless, in this region the yellow bands appear again at identical positions as with \(\gamma\)-ray or deep ultra-violet excitation [Fig. 1(c)]. These two peaks are certainly more prominent than in Fig. 1(b).
CONCLUSIONS

The fluorescence and scintillation spectra for CsI (Tl) show emission bands centred around the same wavelengths. This experimental observation indicates that the fluorescence and scintillation centres are one and
the same. The same fact was also observed for NaI(Tl) and KI(Tl) crystals.

Comparison of Fig. 1 (b) and 1 (c) shows that only a part, i.e., the longer wavelength portion, of the emission spectrum is excited by ultra-violet
light transmitted by $I_2 + CCl_4$ filter, while the complete spectrum appears with $(NiSO_4 + CoSO_4)$. Hence, the luminescence in the range of wavelengths less than $5600 \text{ Å}$ is excited by the wavelengths between $2300 \text{ Å}$ and $3000 \text{ Å}$. The experiments with monochromatic ultra-violet excitation would
probably yield the wavelength at which \( \lambda 4750 \) Å band begins to appear. Thus, the transition energy of the excited state responsible for 4750 Å band would be obtained. Some calculations of the shapes of the potential energy curves for the ground and the excited states to account for the transition energy, so obtained, could then be attempted.

![Graph](image)

As only the yellow bands can be excited by wavelength greater than 3000 Å while the \( \lambda 4750 \) Å band appears when the shorter wavelengths are present in the exciting spectrum, it can be suggested that the excited state for the yellow emission lies in between that for 4750 Å emission and the ground state. It is, of course, assumed that all the optical transitions belong only to one type of luminescence centre, presumably Tl\(^+\) substituting Cs\(^+\). The transition energies corresponding to 5800 Å and 4700 Å emission are roughly 2·1 ev. and 2·6 ev. respectively. The absorption data for CsI (Tl) as given by Pringsheim\(^1\) consists of three peaks centred at 2990 Å, 2690 Å and 2410 Å. The transition energies corresponding to these three peaks are approximately 4·14 ev., 4·6 ev. and 5·14 ev. respectively. Our experiments indicate that the absorption of 2990 Å is responsible for the luminescence emission in the yellow region, with about 2 ev. dissipated in the
Fluorescence and Scintillation Spectra of CsI (Tl) Crystal

crystal corresponding to one yellow photon emission. The correlation between \( \lambda = 4700 \text{ Å} \) emission and the absorption can be established only with the monochromatic ultra-violet excitation experiments.

When Fig. 1 (a) is compared with Fig. 1 (d), we find that the emission spectrum of CsI (Tl) shows a remarkable similarity to that of CsBr (Tl), although the latter shows a peak at 4500 Å instead at 4750 Å. Also from Fig. 1 (f) and Fig. 1 (g), we observe that the emission of NaI (Tl) is almost identical with that of KI (Tl) under ultra-violet excitation both showing a single band centred at 4300 Å. Incidentally, this value agrees fairly well with those given by Birks as \( 4100 \pm 400 \text{ Å} \) for NaI (Tl) and \( 4100 \pm 450 \text{ Å} \) for KI (Tl) and also with the values reported by Milton and Hofstadter\(^3\) as \( 4100 \pm 850 \text{ Å} \) for NaI (Tl) and \( 4000 \pm 600 \text{ Å} \) for KI (Tl) under \( \gamma \)-ray excitation from Ra source.

We note that CsI (Tl) and CsBr (Tl) have a b.c.c. lattice while NaI (Tl) and KI (Tl) are f.c.c. With high concentration of Tl, KCl (Tl) which is also f.c.c. emits a band at 4700 Å.\(^2\) In spite of these differences in details, it appears that the essential structure of the luminescence spectrum depends upon the type of crystal lattice or more precisely on the number and disposition of the nearest neighbours of the substitutional Tl\(^+\) ion. The small differences in the position of the peaks may be attributed to the types, symmetry and distances of perturbing ions.

**SUMMARY**

Fluorescence and scintillation spectra of a single crystal of CsI (Tl) at room temperature excited by ultra-violet (with \( \lambda = 2300 \text{ Å}-3600 \text{ Å} \)) and \( \gamma \)-rays from Co\(^{60}\) respectively are presented. They are continuous in the visible region (4000 Å–6000 Å) with at least three well-pronounced peaks at \( 5950 \pm 50 \text{ Å}, 5700 \pm 50 \text{ Å} \) and \( 4750 \pm 50 \text{ Å} \). There is an indication of a fourth peak at \( 4400 \text{ Å} \). The same peaks appear in both types of excitation. Hence the luminescence centres in the two processes seem to be identical. With the exciting ultra-violet comprising of \( \lambda > 3000 \text{ Å} \), only the two peaks in yellow region appear. Hence, it seems that the excited level responsible for the yellow emission lies in between the ground and the excited state responsible for \( 4750 \text{ Å} \) emission. Luminescence spectra for CsBr (Tl), NaI (Tl) and KI (Tl) are also presented. It is concluded from the comparison of all the spectra obtained that the type of emission spectrum depends on the crystal structure.
ACKNOWLEDGEMENT

The authors wish to thank Professor R. K. Asundi and other members of the Spectroscopy Group in Analytical Division of the Atomic Energy Establishment, Trombay, for the use of their spectroscopic instruments and helpful discussions.

REFERENCES

2. Ibid., 1949, 620.