distance in solid krypton.[3] The formation energy was found to be 0.582 eV, and the formation volume was 0.89 atomic volumes (compared with 0.75 atomic volumes in krypton).

Because electron redistribution effects are not appreciable in the molecular solids, one would expect the vacancy and sublimation energies to be about equal. The ratio E_F/E_S for these calculations is 0.99. For krypton the ratio was 0.98 by calculation[3] and 0.67 by experiment.[1] Losee and Simmons interpret this discrepancy as being probably due to many-body interactions.

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Luminescence of RbI:Tl†

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Emission spectra of RbI:Tl for excitation in A, B, C, and D absorption bands were measured at 4.2, 77, and 300°K. At 4.2°K, four prominent bands are observed at 3.42, 4.24, 2.82, and 2.58 eV. The 3.42- and 4.24-eV emission bands appear most prominently for A and B excitations. They are thus assigned T_{1u} and $T_{2u} \rightarrow A_{1g}$ transitions, respectively. The 2.82- and 2.58-eV bands appear for both C and D excitations. These are also stimulated with high efficiency in the first exciton region of RbI. Both these bands are attributed to the decay of self-trapped excitons adjacent to thallium ions.

INTRODUCTION

SINGLE crystals of alkali halides doped with thallium halides show absorption bands in regions where crystals are normally transparent. Irradiation in these absorption bands normally labeled A, B, C, and D gives rise to emissions characteristic of the thallium ion. Several workers have studied this luminescence.[1–10] Edgerton and Teegarden[6] made detailed measurements of emission spectra in potassium halides. They gave an energy level scheme based on a model proposed by Seitz[11] for interpreting the absorption spectra and assigned specific electronic transitions to various emission bands. Illingworth[7] studied lifetimes and variation of intensity with temperature of some of the emission bands, and gave a quantitative description of the decay of emission for A-band excitation. He also found that four of the emission bands had lifetimes consistent with the model proposed by Edgerton and Teegarden but the decay of the low-energy emission band did not agree with this model. In the case of KI:Tl the two emission bands at 3.69 and 2.88 eV have been assigned to transitions from the Jahn-Teller split components of the T_{1u} level to the ground level by Trinkler and Plyavin.[8] Their measurements were performed at 80°K for irradiation in A band only. Donahue and Teegarden[10] have studied the emission of thallium in potassium halides with emphasis on A and D excitations and have proposed that the lowest-energy emission band is due to self-trapped excitons perturbed by neighboring thallium ions.

Since the thallium ion which enters the lattice substitutionally gives rise to the emission, it should be similar if the host lattice is changed. Sodium iodide doped with thallium has absorption bands similar to potassium halides,[12] but the emission spectra are slightly different. With this in view, the emission spectra of thallium-doped rubidium halides have been investigated. In this paper the results on RbI:Tl are reported. Excitation spectra of some of the emission bands of thallium ion for energies extending into the fundamental absorption region up to 7.5 eV are presented.

EXPERIMENTAL

Single crystals of RbI:Tl were grown by the Kryropolous method in air. Emission spectra were

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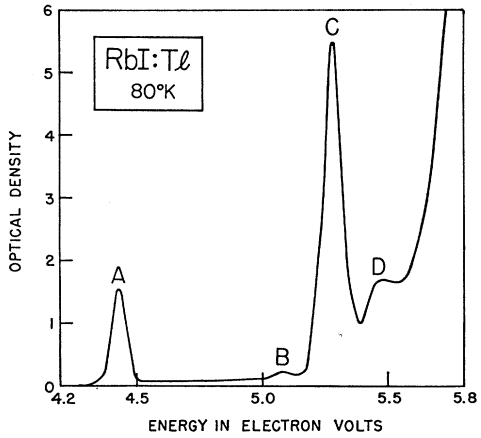

FIG. 1. Absorption spectrum of a single crystal of RbI:Tl at 80°K.

measured with crystals in which the thallium concentration, estimated from the absorption coefficient, varied from 10^{-4} to 10^{-5} mole%.

At low temperatures absorption spectra were measured with a Cary-15 spectrophotometer using a Cary low-temperature cryostat. The samples were cooled by conduction from a copper block attached to the liquid-helium reservoir. When liquid helium and liquid nitrogen were in the reservoir, the estimated temperature of the crystal was 10 and 80°K, respectively.

For recording the emission and excitation spectra crystals were cooled to 4.2 or 77°K by immersing in liquid helium or liquid nitrogen using an Andonian low-temperature cryostat, or they were cooled to 10°K using a conduction cryostat of standard design. Samples were irradiated in the desired region with a Bausch and Lomb high-intensity monochromator (model No. 33-86-25) with a deuterium source. The emission was observed at right angles to the excitation light and analyzed with a Bausch and Lomb monochromator (model No. 33-86-40) and EMI 6256B photomultiplier. The emission spectra were recorded by keeping the excitation monochromator slits open to a bandpass of 25 A and by scanning with the analyzing monochromator, with a bandpass of 66 A. The emission spectra have been corrected for the response function of the analyzing system. The response function was measured using a secondary standard quartz iodide lamp which had been calibrated with an NBS primary standard lamp.

A Seya Namioka vacuum uv monochromator was used to irradiate the crystals while measuring the excitation spectra. In this case the analyzing monochromator was set at one wavelength and the excitation wavelength was changed. The settings and bandpass of the analyzing monochromator was adjusted so that the emission from more than one band due to overlapping was not detected at the same time. The bandpass of the excitation monochromator was 16 A. These spectra were corrected for changes in thespectral output from the source and the excitation monochromator.

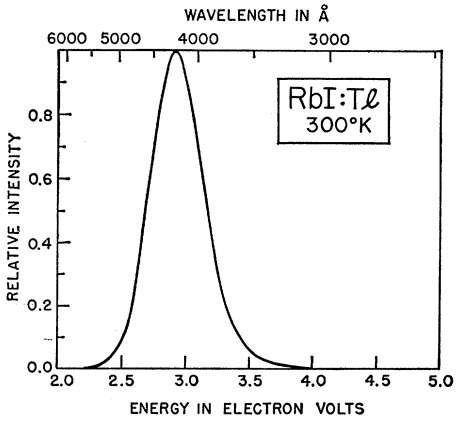

FIG. 2. Emission spectrum of RbI:Tl crystal at 300°K for irradiation in *A*, *B*, and *C* bands.

RESULTS

The absorption spectrum of RBI: Tl at 80°K is shown in Fig. 1. *A*, *B*, *C*, and *D* band peak positions occur at

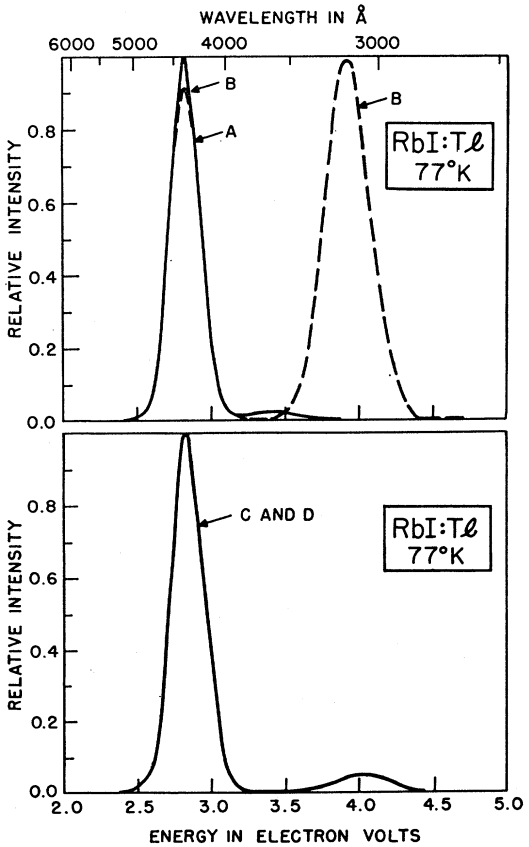

FIG. 3. Emission spectra of RbI:Tl crystal at 77°K for irradiation in *A*, *B*, *C*, and *D* bands.

4.43, 5.08, 5.28, and 5.46 eV. At 10°K the peak positions of these bands are at 4.44, 5.10, 5.29, and 5.46 eV. As in other alkali halides, A band has a tail on the low-energy side. No obvious structure is observable in other bands.

The emission spectrum at room temperature is shown in Fig. 2. At room temperature irradiation in A, B, and C bands gives rise to the same emission. This consists of a single peak at 2.94 eV with a slight tail on the high-energy side. Emission spectra for irradiation in the absorption bands at 77°K are shown in Fig. 3. Strong emission occurs at 2.84 eV for irradiation in all the absorption bands. For B irradiation a band is observed at 3.93 eV in addition to the 2.84-eV emission. Weak emission bands occur at 3.40 and 4.05 eV for A and C and D excitations, respectively, as shown in Fig. 3.

Several new bands appear in emission at 4.2°K. The emission spectra for A, B, C, and D excitation are shown in Figs. 4 and 5. For excitation in the A band, emission is predominantly at 3.40 eV. A twenty times weaker emission is observed at 2.81 eV. B-band irradiation gives rise to five emission bands. The strongest of these is at 4.24 eV. This overlaps the A absorption band. The other bands at 3.97, 3.41, 2.81, and 2.62 eV are all about one-fifth the intensity of high-energy emission. For C-band excitation the same 4.24-eV band appears but with decreased intensity. The strongest band is at 2.62 eV, and two others are at 2.82 and 3.40 eV. For D excitation the strongest peak occurs at 2.58 eV, and

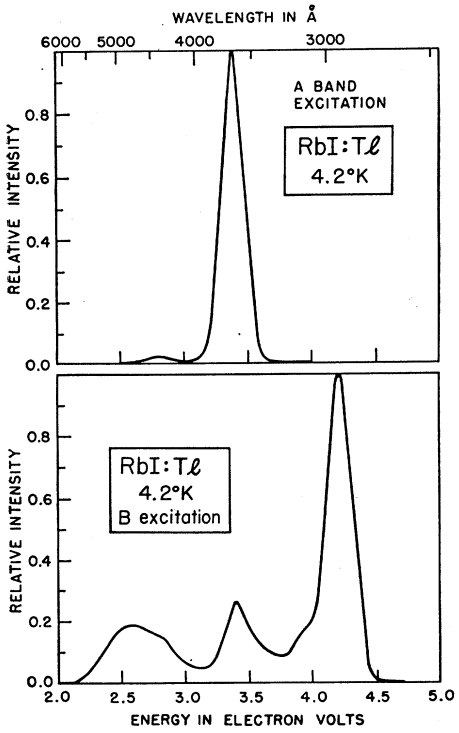

FIG. 4. Emission spectra of RbI:Tl at 4.2°K for irradiation in A and B absorption bands.

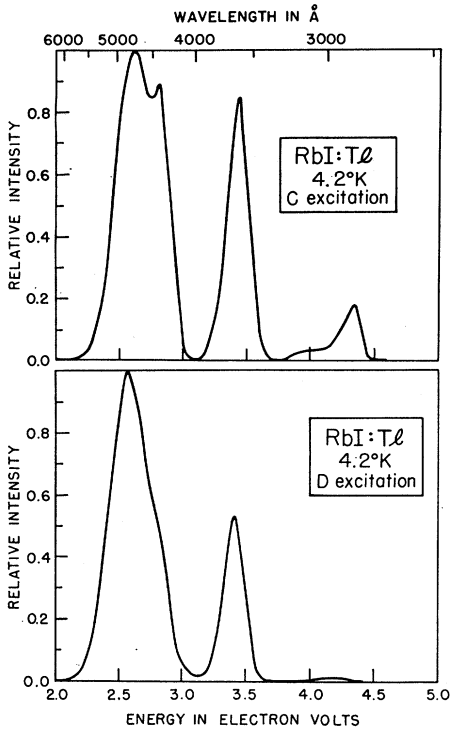

FIG. 5. Emission spectra of RbI:Tl at 4.2°K for irradiation in C and D absorption bands.

two more bands are at 3.40 and 2.81 eV. The latter appears as a shoulder on the 2.58-eV emission. The 4.24 eV-emission is very weak.

The excitation spectrum for the 2.58-eV emission band from 5.2 to 7.3 eV is shown in Fig. 6. It should be noted that the energy range of this spectrum extends well into the intrinsic absorption region of the host crystal. This spectrum has some striking characteristics. Peak positions are observed corresponding to the C and D absorption bands of thallium at 5.28 and 5.46 eV. The emission intensity increases steeply at 5.6 eV and attains a minimum at the position corresponding to the first exciton peak. Luminescence efficiency increases again on the high-energy tail of the first exciton peak. The intensity decreases at 6.20 eV and does not increase at higher energies. The position where the intensity decreases, i.e., 6.2 eV, corresponds to the $n=2$ line of the Wannier exciton series. The band gap in RbI is placed at 6.26 eV. (Though this spectrum has not been corrected for the reflectivity losses from the surface of the crystal, such a correction will not change the basic characteristics of the spectrum.)

Figure 7 shows the excitation spectrum for the 2.81-eV emission band. The peaks at 4.43 and 5.12 eV correspond to the A and B absorption bands. Other features are the same as those in the excitation spectrum for the 2.58-eV emission discussed above. Structure corresponding to various components of the A and C absorption bands is also seen. The excitation spectrum for the

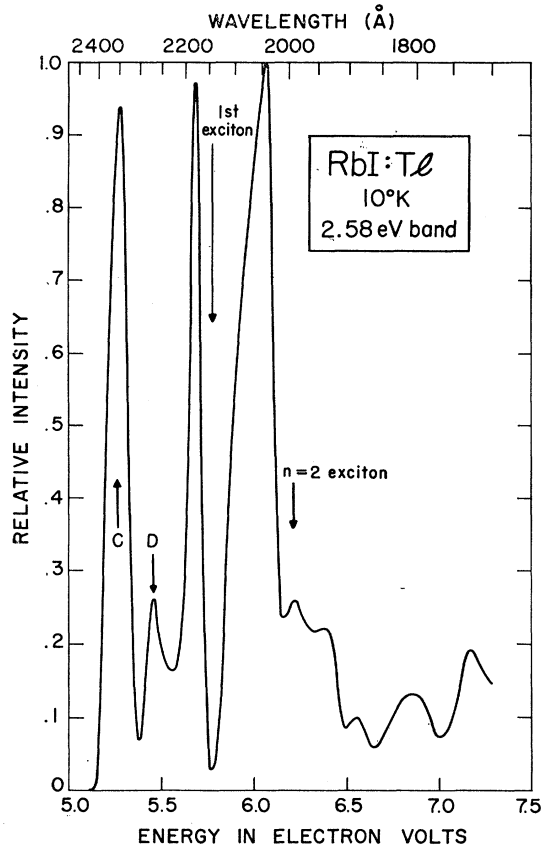

FIG. 6. Excitation spectrum of 2.58-eV emission band (D' band) of RbI:Tl crystal at 10°K.

3.40-eV emission is shown in Fig. 8. Peaks are observed at positions corresponding to C and D absorption bands. The relative intensity of this emission for excitation in the A band (not shown in Fig. 8) would be 6. The minimum at 5.75 eV corresponds to the first exciton peak. This 3.40-eV band is not stimulated with as high efficiency in any part of the intrinsic absorption region of the host crystal as the 2.58- and 2.82-eV emission bands. The rise in intensity on the high-energy side of the first exciton peak in the excitation spectra of 2.58- and 2.81-eV emission bands is temperature-dependent. Above approximately 30°K when the intensity of the 2.58-eV bands decreases the relative intensity of the peak at 5.90 eV (Fig. 7) also decreases. Similarly the peak at 6.04 eV in the excitation spectrum of 2.81-eV emission (Fig. 8) decreases with rise of temperature. It is negligible at 80°K.

DISCUSSION

In discussing the results presented above we will make use of the model proposed by Seitz and used by Edgerton and Teegarden and Illingworth for interpreting the results on potassium halides. The absorption spectrum has four bands. On the Seitz model the A band at 4.44 eV is due to an $A_{1g} \rightarrow T_{1u}$ transition. Optical density of the peak at 5.10 eV decreases by 40% on cooling the crystal from 80 to 10°K, which indicates that it is due to a forbidden transition whose selection rule is overcome by lattice vibrations. As in potassium halides, we assign this to electronically forbidden transition $A_{1g} \rightarrow E_u, T_{2u}$, the separation between E_u and T_{2u} levels being too close to be resolved in absorption spectra. In KI:Tl the B band has been identified[13] to be due to the $A_{1g} \rightarrow T_{2u}$ transition, and we assign the same transition to the peak at 5.10 eV. The C band at 5.29 eV is due to an $A_{1g} \rightarrow T_{1u}$ transition on the Seitz model. The D band which falls on the long-wavelength tail of the first exciton peak cannot be explained on the Seitz model. Yuster and Delbecq have suggested that this band is due to transitions of the valence electrons in halide ions adjacent to the thallium impurity. It is thus a perturbed state of the lowest exciton peak due to the thallium ions.

We will now discuss the emission bands observed by irradiation in the absorption bands discussed above. Figure 9 indicates various absorption bands and corresponding emission bands. For the purpose of discussion we shall designate the emission bands by putting one or two primes on the corresponding absorption band designation, A, B, C, or D. At 4.2°K irradiation in the A band leads to emission almost entirely at 3.40 eV, the emission at 2.81 eV being twenty times less intense than the 3.40-eV band. We therefore assign this emission band to the inverse transition corresponding to the A band, i.e., $T_{1u} \rightarrow A_{1g}$. The 3.40-eV emission band is thus an A' band. Of the five emission bands observed

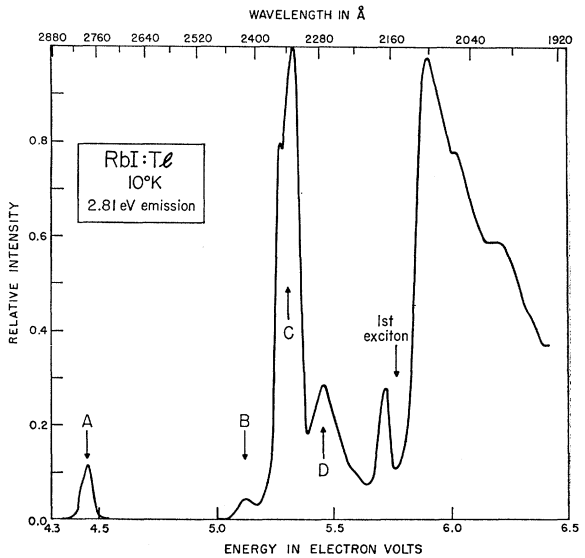

FIG. 7. Excitation spectrum of 2.81-eV emission band (D'' band) of RbI:Tl crystal at 10°K.

[13] R. S. Knox and K. J. Teegarden, in *Physics of Color Centers*, edited by W. B. Fowler (Academic Press Inc., New York, 1968), p. 45.

for B irradiation the most intense one is at 4.24 eV. Since this overlaps the A absorption band, reabsorption causes an A' emission. The 4.24-eV emission occurs with very small intensity for C and D excitations and thus is really characteristic of B-band absorption. We therefore call this the B' band and assign it to the inverse transition corresponding to the B band, i.e., $T_{2u} \rightarrow A_{1g}$. The small 3.97-eV emission occurs for B excitation only, and is therefore assigned to the inverse of the second component of B band transition, i.e., $E_u \rightarrow A_{1g}$ and we designate it as B'' band. On irradiation in the B band the excited electron can decay nonradiatively to E_u state and emit B'' band. The two weak emission bands 2.81 and 2.62 eV are due to thermal transitions to lower levels as discussed below.

We leave the C excitation for the moment and consider D irradiation. Of three emission bands observed, the most prominent one is at 2.58 eV. We thus attribute this D' band to the inverse of the D band transition in absorption. As mentioned earlier the D band is due to an exciton transition perturbed by thallium ions. The D' emission is therefore due to a perturbed exciton transition. The 2.81-eV emission has half the intensity of 2.58-eV emission. This emission is also seen strongly with C excitation but is still less intense than the 2.58-eV emission. Though not excited with maximum efficiency in the D absorption band, the characteristics of the 2.81-eV emission are similar to that of the low-energy emission of KI:Tl. It is the only band emitted at room temperature and is prominently excited in all the four absorption bands at 80°K. It shifts to lower energies as the temperature is lowered. For these reasons it is felt that this band originates from a perturbed exciton transition as discussed by Donahue and Teegarden.[10] It is thus suggested that the emission band at 2.81 eV is also due to a perturbed exciton transition. We shall call this D'' band.

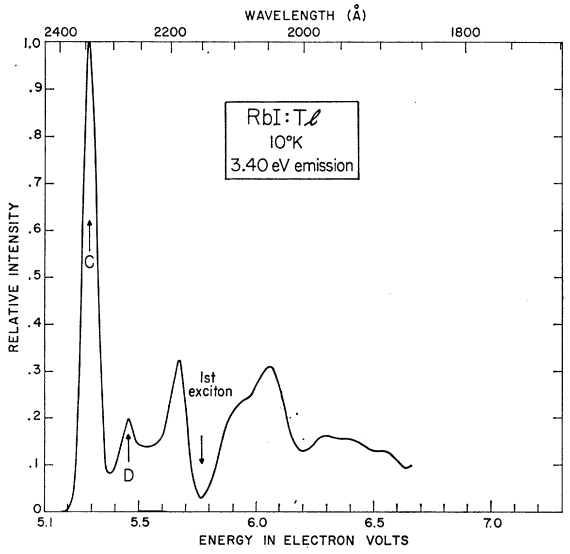

FIG. 8. Excitation spectrum of 3.40-eV emission band (A' band) of RbI:Tl crystal at 10°K. The relative intensity of this emission for excitation in the A band would be 6.

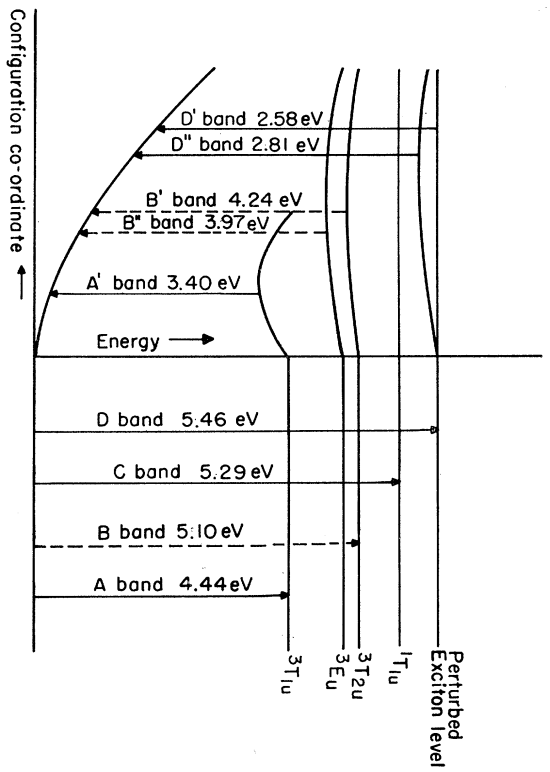

FIG. 9. Diagram indicating the various absorption and emission bands of RbI:Tl crystal.

All five emission bands occur for C irradiation, the A', B', B'', D', D'' bands. In KI:Tl, the C' band is observed on the high-energy side of A band. The corresponding emission does not appear in the present case. It is suggested that in RbI:Tl the center decays thermally to lower energy levels for excitation in the C band.

In a crystal containing thallium ions in substitutional positions, excitons formed by irradiation in the 5-eV region can be self-trapped in two different positions; in normal positions forming $I_2^=$ in an excited state, and in positions next to thallium ions again forming $I_2^=$ in an excited state. In the former case they could give rise to intrinsic emission from self-trapped excitons, and in the latter case they would give rise to emission from self-trapped excitons perturbed by thallium ions. The excitation spectrum for the D' band, Fig. 6, shows that it is stimulated very efficiently in the region of the first exciton peak also, and efficiency falls rapidly in the region where free electrons and holes are formed. This excitation spectrum is qualitatively similar to the excitation spectrum for the 3.15-eV intrinsic emission of rubidium iodide.[14] By irradiation in the D absorption

[14] J. Ramamurti and K. Teegarden, Phys. Rev. 145, 698 (1966).

band the perturbed exciton levels are directly populated and their population decays giving rise to the 2.58-eV emission. By irradiation in the region of the first exciton peak the excitons are trapped adjacent to the thallium ions and they relax into the same level as the perturbed exciton level. This relaxed exciton gives rise to the 2.58-eV emission. Above 6.20 eV, i.e., in regions where free electrons and holes are formed, efficient trapping cannot occur and the emission intensity decreases. The excitation spectrum of Fig. 6 illustrates this effect and supports the argument that the 2.58-eV emission is due to a perturbed exciton state. The excitation spectrum for the 2.81-eV emission is very similar to that of 2.58-eV emission band. This further indicates that this emission originates from the same transitions as the 2.58-eV emission, i.e., from the decay of trapped excitons next to a thallium ion.

At 77°K and room temperature excitation in the thallium absorption bands leads to the 2.84-eV emission which we have attributed to a perturbed exciton transition. This can be explained by the same mechanism as that suggested by Donahue and Teegarden for KI:Tl. The thermal energy available at higher temperatures can cause the hole on the thallium ion to be transferred to a neighboring iodine ion, forming an $I_2^=$ molecule in an excited state next to a thallium ion. At lower temperatures this process and the direct decay of excited thallium levels could both take place giving rise to the thallium emission and the perturbed exciton emission, particularly for C-band excitation.

A feature of the emission bands discussed above is the Stokes shift. For the A' and B' bands this is 1.01 and 0.84 eV, respectively. For D' and D'' bands it is 2.66 and 2.90 eV, respectively. In KI:Tl the D' band has a Stokes shift of 2.65 eV. Large Stokes shifts are also observed in the intrinsic luminescence of alkali halides. As has been pointed out by Knox and Teegarden[13] this occurs because of the large exciton-phonon coupling. Wood[15] has discussed the relaxation process in cubic and V_k-like modes, and his calculations account for the observed Stokes shifts in intrinsic emission. Perturbed excitons would also be strongly coupled to the phonons, and by the same arguments as for the intrinsic emission large Stokes shifts could be expected in the emission from these centers.

The 2.58-eV emission appears only at 4.2°K. In this connection it is interesting to compare what we have called the perturbed exciton emission with the intrinsic emission spectra of RbI.[14] At 80°K two emission bands are observed, one of which is very weak. At 10°K three emission bands are observed. Two perturbed exciton bands at 4.2°K could correspond to two of the three intrinsic emission bands. A third emission band due to perturbed excitons should also be present. This may be at energies too low to be detected by the analyzing system used or it may be of so low intensity that it lies underneath the observed emission bands. In the latter case it may be possible to locate it by fitting the observed emission spectra to specific band shapes.

It should be mentioned here that during the study of intrinsic emission of rubidium iodide it was observed[14] that an emission occurs at 2.64 eV for excitation with 6.05-eV photons. An intensity correction would shift the peak position to 2.58 eV. The data presented in this paper indicate that this emission band is due to unintentional thallium impurity in the rubidium iodide crystals studied.

ACKNOWLEDGMENTS

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[15] R. F. Wood, Phys. Rev. **151**, 629 (1966).