

Excitonic emission from CsI(Na)†

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Photoluminescence in CsI(Na) was studied. This work used nonionizing light sources and obtained the data from well-annealed zone-refined specimens. A series of excitation and emission spectra were measured at temperatures between 300 and 4.2°K. The emission spectra consist of the characteristic blue emission and other low-temperature emissions. The emission spectra were decomposed into the superposition of Gaussian peaks by computer. It is found for the first time that the characteristic emission consists of two bands, centered at 4200 and 3700 Å, respectively. The latter one increased as the temperature decreased. The energies of localized excitons were calculated by employing a Born-Haber cycle. The calculated results were compared with the measured excitation spectra. Each excitation band was identified as the transition of either a free or a localized exciton. The most important one is the exciton created by transferring an electron from an iodine ion to a substitutional sodium ion. This localized exciton called "impurity" exciton is responsible for the excitation band of the characteristic emission. The β exciton also contributes to this excitation at low temperatures. A configuration-coordinate diagram is proposed to explain the evolution of the two characteristic emission bands. The diagram consists of the ground state and two excited states. Two polarization experiments were carried out in order to understand the symmetry of the characteristic luminescent center. Neither of the two characteristic emission bands was polarizable.

I. INTRODUCTION

The luminescence phenomenon in CsI(Na) is interesting both from a theoretical as well as a practical point of view. CsI(Na) is the best alkali-halide x-ray detector now in use.¹ It is also an excellent particle detector that has been used extensively in scintillation studied.¹ Although luminescence in the alkali halides has been studied quite intensively, most of the work has been done on systems with the sodium-chloride structure. Information on the nature of luminescent centers in alkali halides with the cesium-chloride structure and particularly those with nonisomorphic alkali-metal impurities is still limited. This study of the CsI(Na) luminescence will partly fill this gap.

The majority of the previous studies²⁻⁹ in this area introduced ionizing radiations (x-rays, β rays, etc.) and thus produced extra lattice defects in the specimens. Those^{7, 10-13} which excited the specimens with nonionizing ultraviolet light failed to obtain the details of the excitation spectra. There is lacking systematic work on the photoluminescence mechanism in CsI(Na). The conclusions concerning the nature of the luminescent center in CsI(Na) made in the previous works were based on the similarity of the luminescence from CsI(Na) and from CsI doped with divalent cation impurities and deformed CsI crystals. Direct corroboration of those conclusions have not been obtained and ambiguities and controversies still

exist.¹⁴ The work performed on deformed CsI crystals occurred during a period when the effects of trace quantities of sodium were not appreciated. Furthermore, there has not been reported any complete study of the whole emission spectra of CsI(Na) and the correlation among the different emission bands. There is also little published work on the structure of the major emission band of CsI(Na).

In order to resolve these difficulties, we performed a systematic measurement of the excitation and emission spectra of CsI(Na) at temperatures between 300 and 4.2°K. The emission spectra are from 300 to 800 nm with excitations between 300 and 190 nm. The specimens used in the experiment were well-annealed, zone-refined CsI(Na) crystals. The sodium concentration in these crystals is 6 ppm.

Calculations of the localized exciton energies were carried out by employing a Born-Haber cycle. The results were compared with the observed excitation peaks. The origins of these peaks were then elucidated.

The emission spectra were decomposed into the superposition of Gaussian peaks. The luminescent centers responsible for each emission band were identified by the corresponding excitation peaks. A configuration-coordinate diagram was constructed to explain the evolution of the major emission bands of CsI(Na).

In order to understand the symmetry of the major

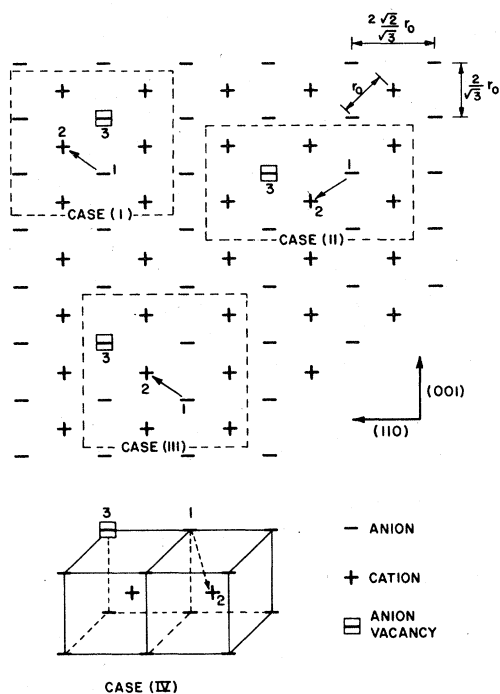


FIG. 1. Charge transfer model for an exciton localized in the vicinity of an anion vacancy.

luminescent center, two polarization experiments were performed. The results helped to postulate the relaxation process of the luminescent center.

Some of our preliminary results have been reported in previous publications.¹⁴⁻¹⁷ Here we present the final experimental results, and the conclusion drawn from them. More details may be found in Ref. 18.

II. CALCULATION OF LOCALIZED EXCITON ENERGIES

Free-exciton absorption peaks have been observed in thin films of both pure CsI and CsI(Na).¹⁹⁻²³ The most commonly observed localized exciton absorption in alkali halides are the α and β bands which are the transitions of the excitons created in the vicinities of a halogen ion vacancy and an F center, respectively. Bassani and Inchauste²⁴ carried out a calculation on the position of the α and β bands relative to the first free-exciton absorption in alkali halides with the sodium chloride structure. This method can be extended to calculate the energy of the excitons located at other defect configurations.²⁵⁻²⁷ It can also be applied to calculate the localized exciton energies in alkali halides with the cesium chloride structure.²⁸ It is important to emphasize that the energies calculated in this manner are good for comparison purposes only and should not be used for absolute energy determinations. We use them

here to distinguish between various configurations.

Figure 1 shows the configurations where an α exciton can be created in CsI. An electron on an iodine ion (called ion number 1) is transferred to a neighboring cesium ion (called ion number 2) in the presence of a nearby iodine ion vacancy (at the position called number 3). The four configurations differ from each other by different relative positions of ions 1 and 2 and the vacancy position. To apply the result given by Bassani and Inchauste²⁴ to the present system, we have to make proper adjustments to fit the crystal structure of CsI. In the sodium chloride structure, each ion has six nearest-neighboring ions of opposite sign. In the cesium chloride structure, this number is eight. The repulsive energy between closed shells of electrons which is part of the potential energy at a lattice point is $\alpha_M \rho e^2 / 8r_0^2$ in the cesium chloride structure and is $\alpha_m \rho e^2 / 6r_0^2$ in the sodium chloride structure.

The other important factors in the calculation are the lattice sums which are defined as

$$S_+ = \sum_{+ions}'' \frac{\cos(r_{2i}, r_{3i})}{r_{2i}^2 r_{3i}^2} - \sum_{+ions}'' \frac{\cos(r_{1i}, r_{3i})}{r_{1i}^2 r_{3i}^2}, \quad (1)$$

$$S_- = \sum_{-ions}'' \frac{\cos(r_{2i}, r_{3i})}{r_{2i}^2 r_{3i}^2} - \sum_{-ions}'' \frac{\cos(r_{1i}, r_{3i})}{r_{1i}^2 r_{3i}^2}, \quad (2)$$

where r_{3i} is the distance between ion i and ion 3, etc. in the units of r_0 , the cesium-iodine ion distance. The summations are over all positive or negative ion sites (as indicated) except that the sites 1, 2, and 3 are omitted as suggested by the triple prime. The values of S_+ and S_- are different in the two alkali-halide crystal structures. To obtain the results in the cesium chloride structure, a method similar to that developed by Rosenstock²⁶ for sodium chloride structure was employed. The numerical work was done on a HP9830 A calculator.

Employing the results given in Ref. 24 and making the suitable adjustments, we obtained the positions of the α excitons at three temperatures. The results are listed in Table I. The first free-exciton energy used in the calculation is 5.57, 5.76, and 5.81 eV at 300, 77, and 4.2 °K, respectively.

TABLE I. Calculated α -band wavelength for the four configurations defined in Fig. 7 at three temperatures.

	Case I	Case II	Case III	Case IV
$h\nu_f - h\nu_\alpha$	0.003	0.109	0.137	0.106
λ_α (Å)	300 °K	2230	2270	2280
	77 °K	2155	2195	2205
	4.2 °K	2135	2175	2185

TABLE II. Calculated wavelengths of excitons localized near a cesium ion vacancy in four configurations defined in Fig. 8 at three temperatures.

$h\nu_f - h\nu_{\text{Cs vac.}}$	Case I	Case II	Case III	Case IV
300 °K	2260	2270	2310	2300
77 °K	2190	2200	2230	2220
4.2 °K	2170	2180	2210	2200

These values were given in Refs. 20, 22, and 23. We measured the same free excitation absorption peaks in thin films of CsI(Na) about 200 Å thick.

The calculation of the energy of an exciton created near a cesium-ion vacancy is similar to that of the α exciton energies.²⁵ The configurations can be represented by Fig. 1 if all the lattice points in the figure change signs. The results are listed in Table II.

Figure 1 can also be used to represent configurations where a β exciton can be created if the iodine-ion vacancies are replaced by the F centers. Again, we employed the formula similar to that given in Ref. 24 and obtained the position of the β bands in CsI at three temperatures. The results are listed in Table III.

Now we consider an exciton created by transferring an electron from an iodine ion which has a sodium ion as one of its nearest neighbors to a cesium ion. The configurations for excitons of this sort can be referred to Fig. 1 if all the lattice points in the figure change signs and vacancies are replaced by sodium ions. The only contribution to the energy difference between a free exciton and exciton in the vicinity of a sodium impurity is the difference of polarization energies of a cesium ion and a sodium ion. The results of $\Delta h\nu$ are case I—0.036 eV, case II—0.027 eV, case III—0.029 eV, and case IV—0.014 eV. The negative value of $\Delta h\nu$ means that the localized excitons have higher energies than the first free exciton. If the energy differences are converted into wavelengths, the differences are about 15 Å. This is within, the experimental error. It is also

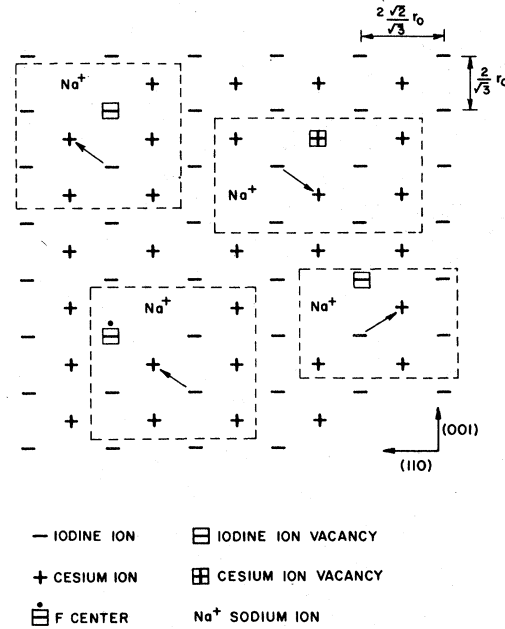


FIG. 2. Some of the possible configurations for an exciton created near a defect complex involving a sodium impurity ion.

worth mentioning here that the numerical values of ionic polarizability of cesium, iodine, and sodium ions from several references²⁹⁻³¹ are different. The variation in the final results of the calculated localized exciton wavelength when the values of ionic polarizability from different sources are used is about ± 20 Å.

The sodium impurity may exist in the neighborhood of a lattice defect such as a vacancy and F center. Figure 2 shows some of the possible configurations for an exciton created near the defect complex involving a sodium impurity ion. The energy difference between the free exciton and a localized exciton of this sort is the sum of the difference of polarization energies of cesium and sodium ions and the quantities given in Tables I—III (with a slight modification of the lattice sums S_+ and S_-) according to the lattice defect involved in the complex. In other words, the effects on the

TABLE III. Calculated energy differences between free and β excitons and β -band wavelengths for the four configurations defined by Fig. 7 at three temperatures.

		Case I	Case II	Case III	Case IV
$h\nu_f - h\nu_\beta$	300 °K	0.451	0.327	0.352	0.198
	77 °K	0.426	0.308	0.332	0.188
	4.2 °K	0.383	0.275	0.297	0.172
λ_β	300 °K	2420	2365	2380	2310
	77 °K	2325	2275	2285	2225
	4.2 °K	2285	2240	2250	2200

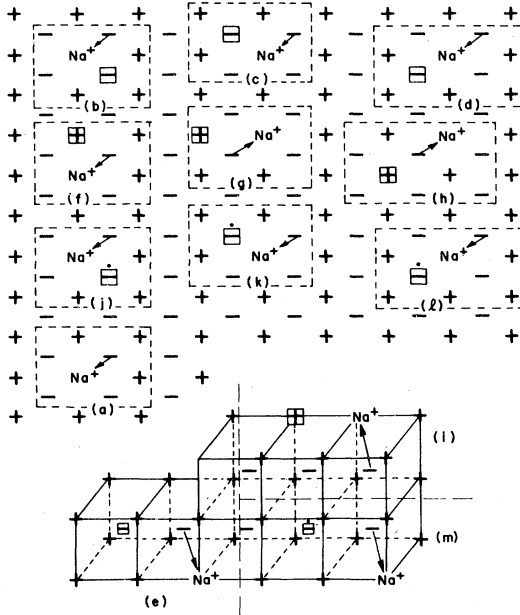


FIG. 3. Several configurations where a sodium impurity exciton can be created near a defect-impurity complex.

localized exciton energy from each individual defect in the complex are additive. For example, the energy difference between the free exciton and the exciton (called β_A exciton) created near an F_A center (an F center with one of its nearest neighbors replaced by a sodium ion) can be expressed as

$$h\nu_f - h\nu_{\beta_A} = (h\nu_f - h\nu_{\beta}) + (h\nu_f - h\nu_{NA}). \quad (3)$$

As indicated in the last paragraph the value of the second term in Eq. (3) is so small that it is impossible to distinguish a β_A exciton from a β exciton in energy.

All the cases discussed above are for localized excitons created by transferring an electron from an iodine ion to a cesium ion in the vicinity of a sodium ion. The sodium impurity ion is not involved in the transition directly but only disturbs the energy states involved in the transition. However, sodium ions are very efficient electron traps,⁸ thus it is very likely that an exciton can be created by transferring an electron from an iodine ion to a sodium ion. We will call this kind of exciton an "impurity" exciton.

The binding energy for an electron trapped on a substitutional sodium ion in CsI has been calculated by Monnier.³² The energy is given by the sum of the difference between the ionization energy of the sodium and the cesium atom and a correction for the fact that the electron at the bottom of the conduction band is delocalized. The result turned out

to be 0.45 eV.

When the sodium "impurity" exciton is created, the energy absorbed by the electron will be 0.45 eV less than when a "host" exciton (i.e., an exciton created by transferring an electron from an iodine ion to a cesium ion) is created in the same configuration. Thus the energy of a sodium impurity exciton in an otherwise perfect lattice is 0.45 eV less than the free-exciton energy. The energy difference between a free exciton and a sodium impurity exciton localized at a defect-impurity complexity can then be expressed as

$$h\nu_f - h\nu_{\text{sodium "impurity"}} = \Delta W + 0.45 \text{ eV}, \quad (4)$$

where ΔW is the energy difference arising from the defect (vacancies, F center, etc.) involved. Figure 3 shows the configurations used to calculate the "impurity" exciton energy. The results are listed in Table IV.

Because ΔW in Eq. (4) is small compared with 0.45 eV except in cases (j)–(m) where an F center is involved in the defect complex, the wavelength of the impurity-exciton bands are almost indistinguishable from each other according to the calculated results.

We should mention at this point that according to Bassani and Inchauspe²⁴ the energy of α excitons should be lower than that of β excitons. However, the results presented here are just the opposite. No satisfactory explanation can be made except that the intuitive statement by Bassani and Inchauspe does not hold for crystals with the cesium chloride structure.

III. EMISSION AND EXCITATION SPECTRUM OF CsI(Na)

The light source used in measuring excitation and emission spectra was a Bausch and Lomb

TABLE IV. Calculated wavelengths of impurity-exciton bands in the configurations defined in Fig. 10 at three temperatures.

Case	300 °K	77 °K	4.2 °K	
a	2420	2335	2315	Impurity exciton
b	2425	2335	2315	Impurity exciton localized
c	2475	2385	2360	near an iodine ion
d	2490	2400	2370	vacancy (impurity α exciton)
e	2475	2385	2360	Impurity exciton localized
f	2465	2375	2355	near a cesium ion
g	2480	2390	2365	vacancy
h	2520	2430	2405	
i	2505	2415	2390	
j	2655	2540	2490	Impurity exciton localized
k	2590	2480	2440	near an F center
l	2600	2490	2450	(impurity β exciton)
m	2520	2420	2390	

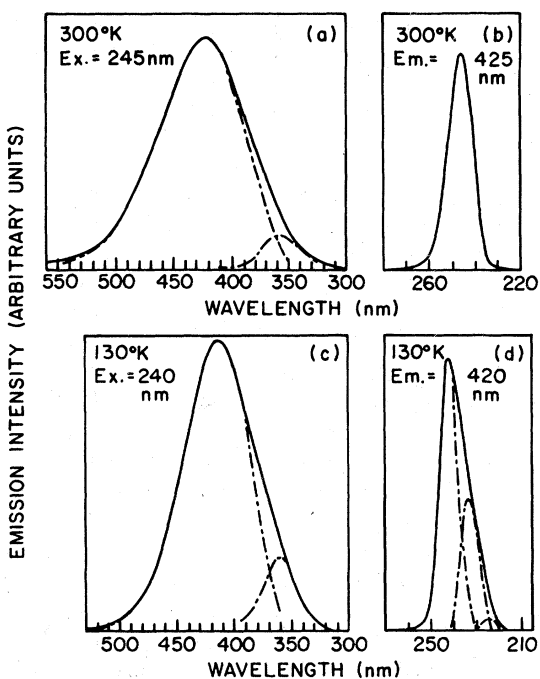


FIG. 4. Characteristic luminescence spectra of CsI(Na) at 300 and 130 °K. (a) Emission spectrum at 300 °K with 245-nm excitation; (b) excitation spectrum at 300 °K for the emission at 425 nm; (c) emission spectrum at 130 °K with 240-nm excitation; (d) excitation spectrum at 130 °K for the emission at 420 nm.

deuterium lamp. The photomultiplier was a RCA 8645 with S-20 spectral response.

The excitation spectra cover the range from 2000 to 3000 Å. Some were extended to 3500 Å. The emission spectra are measured from 3000 to 5000 Å. The emission spectra were corrected for the spectral response of the photomultiplier tube. The corrected emission spectra were analyzed by a least-squares fitting program on a PDP-10 computer. The numbers, positions, heights, and widths of Gaussian peaks whose superpositions fit the emission spectra best were determined. The decomposition of the excitation spectra was done by observation. A series of excitation spectra of adjacent emission wavelengths were taken. The evolution of the excitation bands was revealed by comparing these excitation spectra.

A. Characteristic emission and excitation spectrums of CsI(Na) crystals

The major emission from bulk crystals of CsI(Na) when excited with ultraviolet light or ionizing radiations is blue light with λ_{\max} around 4200 Å.^{11,12} In a preliminary experiment¹⁶ we found that this blue emission was absent in thin films of CsI(Na) about 200 Å thick and was very

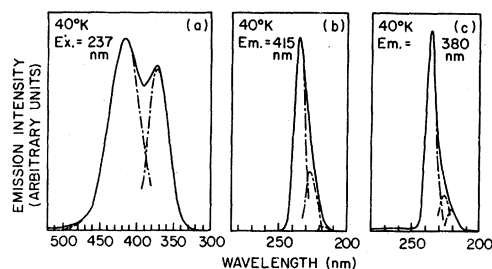


FIG. 5. Characteristic luminescence spectra of CsI(Na) at 40 °K. (a) Emission spectrum of CsI(Na) crystal at 40 °K with 237-nm excitation; (b) excitation spectrum at 40 °K for the emission at 415 nm; (c) excitation spectrum at 40 °K for the emission at 380 nm.

weak compared with the intrinsic emission of pure CsI at liquid-nitrogen temperature in thin films about 6000 Å thick. It was also found that the emission and excitation spectrums were modified by the heat treatment the specimens received before the optical measurement. In order to avoid the influence of the heat treatment and to elucidate the effect of the sodium impurity on the luminescence properties of CsI(Na), it is necessary to perform the measurement on CsI(Na) bulk crystals which have never been irradiated before the measurement and whose defect concentration (other than the desired impurity content) is low.

Figures 4–6 are the major emission and the corresponding excitation spectra taken from CsI(Na) crystals of this sort at several temperatures. The dash-dot curves in the emission spectra are the Gaussian peaks fitted by the computer analysis. That in the excitation spectra were fitted by observation. The most striking point of the measured emission spectra is that they actually consist of two bands, one peaking around 4200 Å and the other one around 3700 Å. This feature has not been reported before.

The peak position of these two emission bands

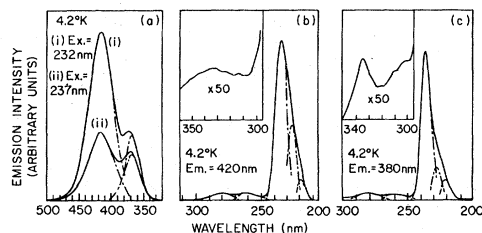


FIG. 6. Characteristic luminescence spectra of CsI(Na) at 4.2 °K. (a) Emission spectrum of CsI(Na) crystal at 4.2 °K with excitation at (i) 232 nm; (ii) 237 nm; (b) excitation spectrum at 4.2 °K for the emission at 420 nm; (c) excitation spectrum at 4.2 °K for the emission at 380 nm.

varied within a 100-Å range. It is difficult to tell whether this variation is due to the nature of these emission bands or is due to the interference with other emission bands and the uncertainty of the computer analysis. The half width of the 4200-Å band is 0.64 eV at 300 °K and gradually decreased to 0.33 eV at 4.2 °K. The halfwidth of the 3700-Å band lies within the range from 0.33 to 0.24 eV at different temperatures. However, because the error of the computer result in peak half width is about 0.15 eV this variation is within the error range. It is difficult to establish a well-defined relation between the temperature and the half width of the 3700-Å emission band.

The intensity of the high-energy peak relative to that of the low-energy one increased about 4.5 times as the temperature decreased from 300 to 4.2 °K. The relative intensity also depended on the excitation energy. This point will be discussed later. The data showed that the emission intensity did not change much with temperature when the crystal was excited at the peak of the corresponding excitation spectrum. The intensity had small variations at different temperatures which may be due to the slightly different alignments of the instruments between measurements.

The excitation spectrums of this characteristic emission shifted toward higher energies as the temperature decreased. At 300 °K the excitation spectrum is a single peak centered at 2450 Å. There is no difference between the excitation spectrums of the 4200- and 3700-Å emission band. This possibly results from the low intensity of the 3700-Å band at this temperature. In fact, the contribution to the intensity at 3700 Å from 4200-Å band is even higher than that from the 3700-Å band. It is impossible to separate these two emission bands from each other in measuring the excitation spectrum. Thus, when we set the monochromator on the emission side at 3700 Å and measured the corresponding excitation spectrum at room temperature, we were essentially measuring the excitation spectrum of the 4200-Å band. As the temperature decreased, the excitation spectrum deviated from a single Gaussian peak. At 130 °K the excitation spectrum peaked at 2400 Å. However, it can be decomposed into the superposition of three Gaussian peaks centered at 2400, 2325, and 2250 Å, respectively. When the crystal was excited at the two higher-energy bands, in addition to the characteristic emission, other emission bands were also observed which will be discussed in the next section. The intensity of several weak excitation bands with wavelengths longer than 2500 Å increased as the temperature decreased. The peak position of the three Gaussian bands shifted gradually to 2320, 2250, and 2170 Å at 4.2 °K for the

4200-Å emission. The lowest-energy peak is located at slightly longer wavelengths (about 15 Å) for the 3700-Å emission. The difference between the relative intensities of these two emission bands at 4.2 °K when the crystal was excited at 2320 and 2370 Å clarifies part of this feature [Fig. 6(a)]. The intensities of the two higher-energy excitation bands relative to the major (i.e., the lowest-energy) peak of the 3700-Å emission were lower than that of the 4200-Å emission. From Figs. 6(b) and (c) we can also see the different structure at the long-wavelength tail of the excitation spectra of these two emission bands.

At this point we will turn our attention to other emission bands which were observed at low temperatures and try to identify their origins. This will hopefully clear up some of the controversial points about the luminescent nature of CsI(Na).

B. Other emission bands and their origins

In addition to the characteristic blue emission, we measured several other emissions from CsI(Na) at low temperatures. These emissions were weak compared with the major one and generally speaking, their intensities increased as temperature decreased. The corresponding excitation spectra were closely related to the excitonic absorption spectra. We will try to identify the origins of these emissions by comparing the excitation energies and the excitonic bands calculated in Sec. II.

It has been observed³³⁻³⁵ that at temperatures between 20 and 140 °K, pure CsI has an emission peaking at 3380 Å when the crystal is excited in the free-exciton bands. At liquid-helium temperatures, this excitation also yields an emission band centered at 2900 Å whose intensity decreases rapidly with increasing temperature and is unmeasurable above 25 °K. In our experiment, we observed an emission band around 3450 Å when the crystal was excited in the free-exciton region. However, this emission was not isolated from other emissions, such as the characteristic emission of CsI(Na). This is understandable because the blue emission can also be excited in the free excitonic bands as shown by the excitation spectrums in Figs. 4-6. Figure 7 gives the emission spectrums at several temperatures when the crystal was excited in this region. Figure 8 is the corresponding excitation spectrums. The highest excitation peak is the one due to the characteristic emission because this blue emission extended into the 3450-Å region. The arrow in the figure indicates the peak of our interest at this point.

We did not observe the 2900-Å emission as reported in Ref. 36. At temperatures below 25 °K,

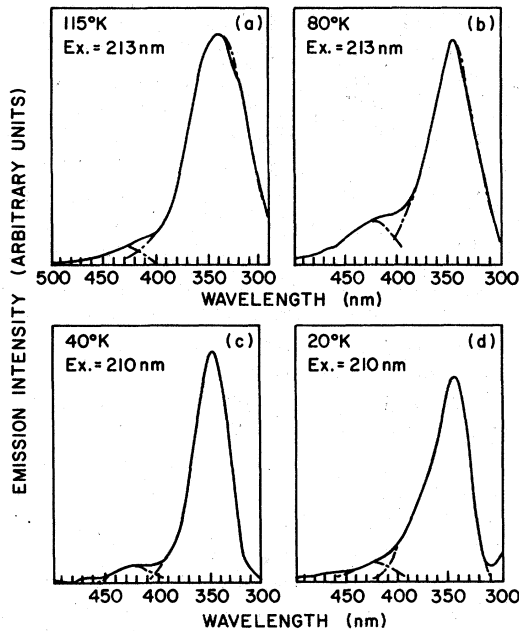


FIG. 7. The 345-nm emission band of CsI(Na) at various temperatures: (a) at 115 °K, excited at 213 nm; (b) at 80 °K, excited at 213 nm; (c) at 40 °K, excited at 210 nm; (d) at 4.2 °K, excited at 210 nm.

there are several excitation bands [Figs. 6, 8, 10, and 12(b)] for all emissions and also absorption bands around 2600–2900 Å. Furthermore, the photomultiplier tube used in the experiment has very low sensitivity in this regions. Thus it is very possible that this emission was reabsorbed by the crystal and excited other emissions and could not be detected.

However, there was another emission band peaking around 3100 Å which appeared at temperatures below 130 °K. Figure 9 shows this emission spectrum at several temperatures. The excitation peak for this emission was located at a lower energy than that for the 3450 Å. This can be seen comparing the excitation energies in Figs. 8 and 9. Figures 10(a) and 10(b) are the excitation spectra of the 3100- and 3450-Å emissions at two temperatures. Again the peaks of our interest at this point are indicated by arrows. At 4.2 °K, the excitation peak at about 2200 Å was greatly reduced while the low-energy bands increased drastically. Figure 10(c) shows the excitation spectra of emission at 3100 and 3400 Å at 4.2 °K.

The 3450-Å emission has been attributed to the radiative recombination action of relaxed free excitons. The 3100-Å emission whose excitation energy is right below that of the 3450-Å emission can then be assigned to the recombination of relaxed "host" α excitons because the host α exciton

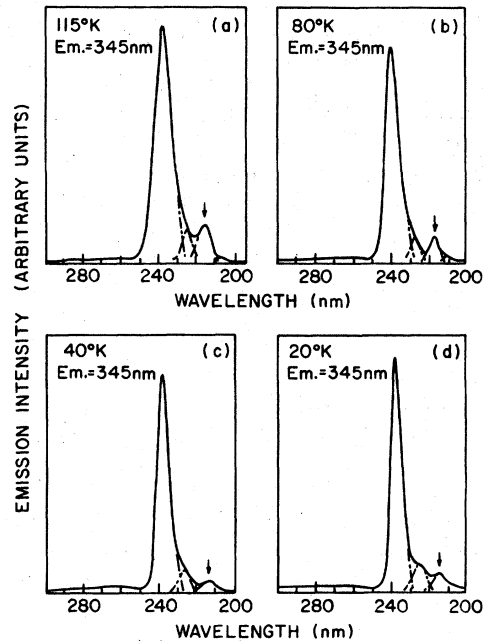


FIG. 8. Excitation spectra of the 345-nm emission band at (a) 115, (b) 80, (c) 40, (d) 20 °K.

has its energy right below the first free exciton as shown in Sec. II. This assignment is further confirmed by the same temperature dependence of the α band absorption and the 3100-Å emission, i.e., both of them started to show up at 130 °K and

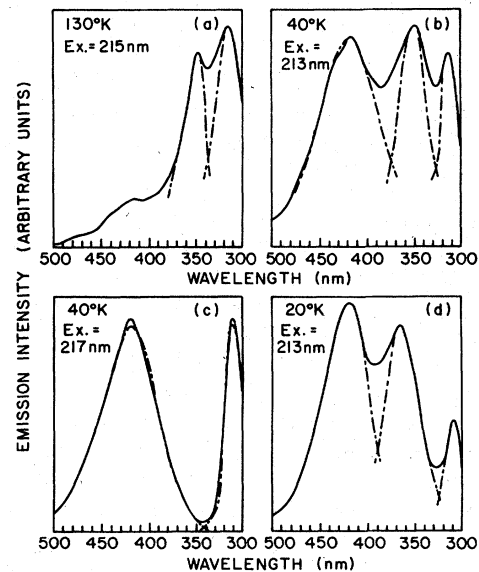


FIG. 9. Emission spectra of CsI(Na) containing the 310-nm emission band: (a) at 130 °K, excited at 215 nm; (b) at 40 °K, excited at 213 nm; (c) at 40 °K, excited at 217 nm; (d) at 20 °K, excited at 213 nm.

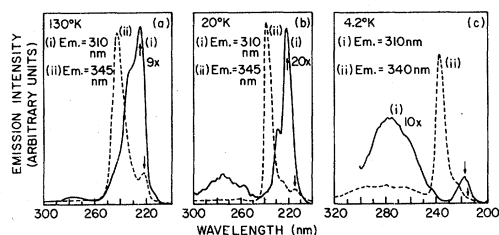


FIG. 10. Excitation spectra of the 310-nm emission in comparison with that of the 345-nm emission at (a) 130, (b) 20, and (c) 4.2 °K.

disappeared below 20 °K. The disappearance of the α excitation can be explained in the following way: At temperatures below 20 °K the defect density was so high that defect clusters or complexes were formed. Thus the α band decreased rapidly while the long-wavelength tail of the excitation spectra which is due to the excitons localized near the defect cluster or specimen surface increases drastically.

When the CsI(Na) crystal was excited in the long-wavelength region mentioned above at 4.2 °K, the strongest emission band was located at 4500 Å, together with other weaker bands. This emission was observed at temperatures below 100 °K; however, the intensity was not strong enough to give a well-defined spectrum until 20 °K. Figures 11 and 12 are the emission and excitation spectra of this emission at 20 and 4.2 °K. For comparison, those of the characteristic emission are also shown in these figures. Figure 12 shows that the major excitation peak of the long-wavelength side of the 4500-Å emission was located at a slightly lower energy than that of the 4200-Å emission. Figure 11 clearly shows that the 4500-Å is a new low-temperature emission and should be distinguished from the characteristic emission. Furthermore, the

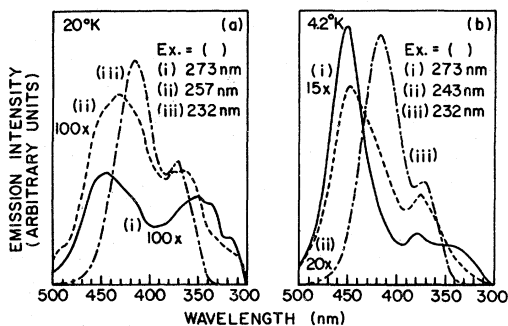


FIG. 11. Emission spectra showing the evolution of the 450 nm band in terms of excitation energy at (a) 20 °K with excitation at (i) 273, (ii) 257, (iii) 232; and (b) 4.2 °K with excitation at (i) 273, (ii) 243, (iii) 232 nm.

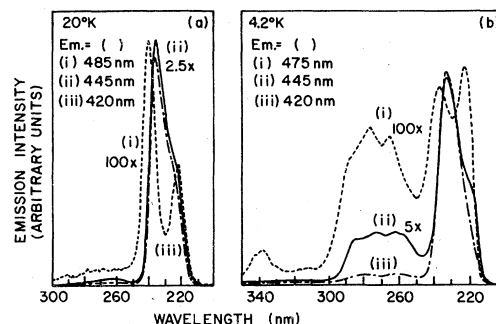


FIG. 12. Excitation spectra of the peak and the long-wavelength side of the 445-nm emission band in comparison with those of the characteristic emission band at (a) 20 °K; (b) 4.2 °K.

major excitation peak at 2400 Å is not the residue from the characteristic emission as in the case of the 3450-Å emission, while the one at 2200 Å is the residue because the emission spectrum of CsI(Na) with this excitation did not show any trace of the 4500-Å emission band (Fig. 13). In view of the excitation energy and the temperature dependence, the 4500-Å emission can be well described as the radiative recombination of relaxed excitons localized near the defect cluster and the "impurity" α and β excitons. The latter two dominated at temperatures above 4.2 °K.

The long-wavelength tail appeared in the excitation spectrum of all the emission bands at low temperatures. Since these excitation bands are in the same region of the absorption as that due to excitons localized near defect clusters (below those in Sec. II), the configuration around the luminescent centers created by this excitation should be complicated. We hypothesize that after the excitation the lattice around the center could relax into any of the configurations which were the same as those around the centers created by higher-ener-

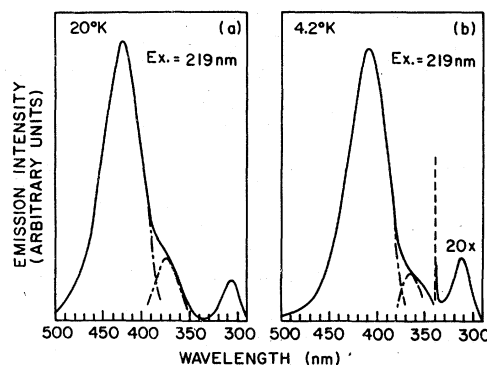


FIG. 13. Emission spectra of CsI(Na) excited at 219 nm at (a) 20 °K; (b) 4.2 °K.

TABLE V. Luminescent peaks of CsI(Na) found in this work and the related excitons.

Emission peak (Å)	Corresponding excitons	Temperature range
4200	Impurity exciton	All temperatures
	Host β exciton	Low temperatures
3700	Impurity exciton	All temperatures stronger at low temperature
3450	Free exciton	Low temperature
3100	Host α exciton	Low temperature
4500	Impurity α and β excitons	Low temperature

gy excitation. The excitons then recombined and gave the same emission as those excited by the higher-energy bands. The complexity of the emission spectrums under this low-energy excitation reveals the complexity of the corresponding luminescent centers. Table V lists all the luminescence peaks found, and the related excitons.

C. Emission polarization experiment

In order to understand the structural symmetry of the luminescent centers in CsI(Na) and thus help to make conclusions concerning the luminescence mechanism in CsI(Na) two emission polarization experiments were carried out.

The first polarization experiment was designed to find out the relation between the polarization of the excitation and emission light. The sample used in this experiment was a single crystal of cesium iodide doped with 6-ppm sodium which was cut and polished along (100) faces. The exciting light fell on the (010) face and the emitted light was observed at right angles to the (001) face. Ultraviolet-visible linear polarizers from Ealing were used to polarize the exciting light and to analyze the emission. A filter was used to separate the 4200- and 3750-Å emission. The reason for using a filter instead of using a monochromator is that the monochromator is able to produce a polarization as much as 0.3 $[(I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp}) = 0.3]$. This effect could account for the polarization artifact reported by Edgerton³⁶ who measured the polarization of the emission from KI(Tl) with a similar arrangement but used a grating monochromator in the emission side. A neutral density filter was inserted in front of the photomultiplier tube in order to cut down the light input into the tube and thus to avoid saturating the tube.

The excitation light was polarized with the electric along [100], [001], and [101] directions. In each case, the polarization of the emission light was measured by rotating the polarizer in the emission side and the emission intensity was re-

corded for every 10°. The crystal was held at 4.2 °K during the measurement. Neither the 4200- nor the 3750-Å emission band showed any polarization. Although there was a small variation (about 5%) of the emission intensity as the emission polarizer rotated, this variation was independent of the excitation polarization and thus was believed due to the slight misalignment of the optical components. The polarization of the whole characteristic emission (i.e., without the filter) was also measured and the same result was obtained. We then conclude from this experiment that the characteristic emission of CsI(Na) is nonpolarizable.

The second polarization experiment was designed to find out whether the V_k center is directly associated with the characteristic luminescence of CsI(Na). It has been found that in CsI(Na) crystals having aligned V_k centers in a [100] direction, the intrinsic recombination luminescence at 290 m, and 340 nm produced by optical excitation of the traps exhibits a partial plane polarization having essentially a σ character with respect to the axis of the parent V_k center $[P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp}) = 0.2]$. Thermoluminescence of CsI(Na) crystals α or β irradiated at 4.2 °K showed that the characteristic emission is the radiative recombination of V_k centers with the trapped electrons.⁸ It is then of interest to see whether V_k centers are produced in CsI(Na) crystals under ultraviolet irradiation and then involved in the characteristic luminescence process via the emission polarization measurement. The single crystal of CsI(Na) which was cut and polished along the (100) faces was kept at 20 °K which is below the V_k center migration temperature.⁸ The crystal was illuminated simultaneously with chopped ultraviolet light at 2350 Å where the peak excitation of the characteristic emission is located at 20 °K and constant intensity blue light at 4100 Å where the V_k absorption band is located. The blue light was polarized along the [100] direction. The blue and ultraviolet lights were incident upon the two large (010) faces of the specimen from opposite directions. The emission light was measured at right angles to the exciting and aligning lights from the (001) face. As would be expected, scattered 4100-Å blue light caused a signal to appear in the output of the lock-in amplifier even when the crystal was not luminescing. To correct for this, the scattered light was measured with the ultraviolet light off. The result showed that the scattered light was very weak, only about 1% of the luminescence intensity. The background of scattered light determined in this way was subtracted from the readings taken with the ultraviolet light on.

Presumably if V_k centers were produced under the 2350-Å excitation, they would then be aligned

by the polarized 4100-Å light along [010] and [001] axes. The electrons recombining with the aligned V_k center would yield an emission polarized in the same directions. In other words, if the V_k centers were produced by the 2350-Å irradiation and were involved in the luminescence process, with the experimental arrangement, we would have measured the characteristic emission light polarized along the [010] direction. The result we obtained was negative. Neither of the two major emission bands was polarized.

Assuming that the 2350-Å light is in the localized exciton region and does not have enough energy to produce stable hole and electron centers, we then tried producing V_k centers by ultraviolet light in the free-exciton region. The crystal was illuminated simultaneously with chopped 2100-Å ultraviolet light and polarized 4100-Å blue light of constant intensity at 20 °K for 10 h. The excitation monochromator was then shifted to 2350 Å while the alignment monochromator was still maintained at 4100 Å. The emission polarization was measured and again the result was negative. No polarization of the characteristic emission was found.

The result of the first polarization experiment shows that there is no correlation of polarization between the characteristic exciting and emitted radiations. This result suggests that the exciton created by the characteristic exciting band loses the memory of polarization if there is any during the relaxation process. The result of the second experiment suggests that isolated V_k centers and trapped electrons are not formed in CsI(Na) under ultraviolet light.

D. Photoluminescence mechanism in CsI(Na)

We shall now attempt to identify the luminescent center in CsI(Na) crystals which is responsible for the characteristic blue emission. The peak excitation energy of this emission agrees very well with the "impurity" exciton energy. It is natural to ascribe this emission to the radiative recombination of a relaxed impurity exciton. However, on the other hand, the calculated energy of the host β exciton has energy only slightly higher than that of the impurity exciton. Moreover, the excitation spectrum of this emission consists of three closely spaced Gaussian peaks. It¹³ has been found that the CsI crystals containing the divalent impurity cations Ca^{2+} , Sr^{2+} , Ba^{2+} , and Mn^{2+} and deformed pure CsI crystals have luminescence properties similar to that of CsI(Na). It is obvious that a sodium impurity exciton cannot be the origin of the luminescence in the divalent impurity-doped crystals. The assignment of the characteristic emission as due to sodium impurity excitons then needs further

consideration.

To solve this difficulty, it is worthwhile to consider the effect of the heat treatment the specimen received before the emission measurement. It has been mentioned at the beginning of this section that the heat treatment modified the excitation spectra of the blue emission CsI(Na). Figure 14 shows the excitation spectrum of two specimens at liquid-nitrogen temperature. Type-I crystal is the crystal which did not receive any heat treatment before the emission measurement. Type-II crystal had been heated to 500 °C, kept at that temperature for 1 h, and cooled to room temperature within 4 h before the measurement. It is expected that type-II crystals have much higher vacancy concentrations than type-I crystals. The excitation spectrum of the type-I crystal has a peak at 2380 Å and a shoulder at 2300 Å. For the type-II crystal, the excitation spectrum is a single peak at 2315 Å which is evidently the same band as the 2300-Å shoulder in the excitation spectrum of the type-I crystal. This result shows that the CsI(Na) crystal which has a higher vacancy concentration has a excitation spectrum different from that of a crystal with a low vacancy concentration.

Another fact that will help is that the excitation spectrum of the blue emission from a mechanically deformed pure CsI crystal or CsI crystal with 1-ppm sodium impurity (which is lower than that for optimum luminescence efficiency, i.e., 6 ppm) has the same character as that found in the excitation spectrum of the type-II crystal (heat-treated) crystal. The excitation peak of the deformed pure CsI crystal is located at a wavelength about 100 Å shorter than that of the undeformed crystal with 6-ppm sodium content.¹⁵ The crystal with 1-ppm sodium content which had a weak emission at 420-

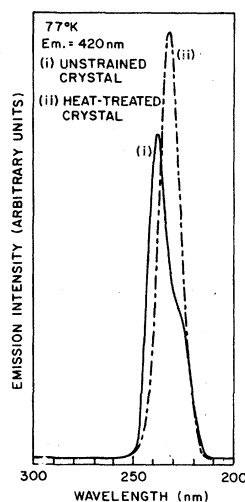


FIG. 14. Excitation spectra of the 420-nm emission band at 77 °K from (i) a well-annealed zone-refined CsI(Na) crystal; (ii) a CsI(Na) crystal which had been heated to 500 °C, kept at that temperature for 1 h and cooled to room temperature within 4 h.

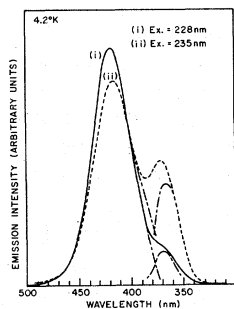


FIG. 15. Emission spectra of CsI(Na) at 4.2 °K with excitation at (i) host β excitonic band at 228 nm; (ii) impurity excitonic band at 235 nm.

430 nm before deformation exhibited a very intense emission centered at 425 nm after deformation while the excitation peak shifted 100 Å toward shorter wavelength.¹⁵

The characteristic emission of CsI(Na) consists of two bands centered at 3700 and 4200 Å, respectively. The former one increases as temperature decreases. The existence of this emission band is not observed in the strained or divalent cation-doped CsI crystals. Furthermore, the excitation spectrums of the two bands are not completely the same. The relative height of the 2280-Å band to the 2320-Å band at 4.2 °K for the 3700-Å emission is lower than that for the 4200-Å [Figs. 6(b) and 6(c)]. When the crystal was excited at 2280 Å at 4.2 °K the intensity of the 3700-Å band was low. Figure 15 clarifies this fact.

We now recall that the calculated results in Sec. II showed that the energies of the host β excitons created in four different lattice configurations are slightly higher than that of the impurity exciton. It is then clear that the major excitation peak of the CsI(Na) crystal with 6-ppm sodium content is due to the impurity exciton while the one at slightly shorter wavelength which is the major peak in heat-treated or mechanical-deformed crystal is due to host β excitons.

The characteristic excitation spectrum of the zone-refined CsI(Na) crystal at room temperature is a single Gaussian peak which according to the discussion above is due to an impurity exciton. At lower temperatures, both of the bands due to impurity excitons and host β excitons exist in the excitation spectrums. As discussed in Refs. 18 and 34, *F* centers can be created in CsI crystals by cooling due to thermal mismatch between the crystal and the sample holder in the Dewar used in the experiment. The low intensity of the β excitation band for the 3700-Å emission and the fact that the 3700-Å emission is missing from the deformed and divalent cation-doped CsI crystals are also consistent with each other.

The ambiguity about the assignment of the characteristic blue emission to the radiative recombination of sodium impurity exciton is then re-

moved. Although the blue emission of the heat-treated or mechanically deformed CsI crystals has the same peak position as that of the CsI(Na) crystal, the composition of the emission spectrums and of the corresponding excitation spectrums are different in details. The blue emission in the strained CsI crystal is then ascribed as due to the recombination of host β excitons. This host β excitation also contributes part of the 4200-Å band from CsI(Na) crystal at low temperatures but not the 3700-Å band.

The emission polarization shows that isolated electron and hole centers are not necessarily formed by ultraviolet light. The recombination of relaxed impurity excitons is direct. Charge transfer and defect diffusion are then not involved in the luminescence process. Lack of or small temperature dependence of the peak emission intensity also suggests this.

The configuration diagram shown in Fig. 16 explains schematically the evolution of the two observed components of the characteristic emission. Excitation in the sodium impurity excitonic absorption band is followed by a relaxation to the first relaxed state (I) of the localized exciton, which exhibits the emission at 3700 Å. The second relaxed excitonic state (II) is reached over an energy barrier E_1 . The emission from this level gives the 4200-Å emission component. The value of E_1 can be determined by the temperature dependence of the quantum efficiency of the 3700-Å emission band which was not measured in our experiment. However, because the 4200-Å emission band is not quenched even at 4.2 °K, the value of E_1 should be very small. E_1 is estimated to be in the order of 10^{-4} eV. There is a possibility that the relaxation of the second excitonic state (II) will lead to a nonradiative transition to the ground state at high temperature. This high-temperature quenching phenomenon has not been observed in the temperature range from 4.2 to 300 °K in our experiment. It is then expected that the energy barrier E_2 for the nonradiative transition should be high at least in the order of 10^{-1} –1 eV if it exists. The dotted part of the ground and the second ex-

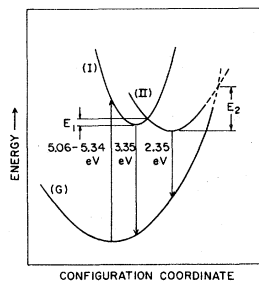


FIG. 16. Configuration coordinate diagram which explains the evolution of the two bands of the characteristic emission.

citonic state in the configuration diagram indicates that the structure there is still questionable.

The lifetime of the characteristic emission of CsI(Na) crystals has been measured by Maumenko and Panova³⁷ and Bates.³⁸ For an increase in the temperature from 80 to 300 °K, the lifetime decreases exponentially from 4 to 0.4 μ sec. This temperature dependence of lifetime can be explained by the double-band feature of the emission. Each of the excited states is characterized by a decay time. At room temperature the majority of the emission comes from the transition from the second excited state (II) to the ground state. The lifetime of the emission at 300 °K is determined by the decay time of the second excited state (II). At low temperatures the emission consists equally of the transition from the two excited states to the ground state, the lifetime of the emission then depends on the decay time of both excited states. Reference 39 gives a complete treatment of a similar problem on intrinsic emission of CsI.

IV. CONCLUSION

Our approach to the luminescence center in CsI(Na) whose conclusions are directly based on the excitonic energies appear to work quite well.

The CsI(Na) crystal exhibits a strong blue emission under ultraviolet excitation. In our measurement, it is the first time that this characteristic emission is found to consist of two components, centered at 4200 and 3700 Å, respectively. The latter one increases as temperature decreases. The comparison of the calculated localized exciton energies and the excitation spectra leads us to the conclusion that the characteristic emission is the radiative recombination of relaxed sodium impurity excitons. The evolution of the two components in this emission can be explained by a configuration coordinates diagram.

It is also concluded from the excitation spectra that the blue emission from a strained pure CsI

crystal and divalent cation-doped CsI crystal is due to the recombination of relaxed host β emission also contributes to the 4200-Å band in the CsI(Na) crystal emission, but not to the 3700-Å band.

The other emission bands which occur at low temperature can be attributed to the recombination of the excitons localized at different lattice defects. Again, these conclusions are based on the excitation energies of the emissions.

The importance of excitation spectra in understanding the luminescence phenomenon is clearly demonstrated by this work. It is regrettable that in many luminescence studies, details of excitation spectrums were not available.

The configuration coordinates diagram proposed in this work which consists of a ground state and two excited states is not complete. The interaction between the second excited state (II) with the ground state needs more investigation. To elucidate this interaction, the emission and excitation measurement should be extended to temperatures higher than 300 °K. However, caution must be taken as the CsI crystal will undergo a structure transformation at high temperatures.

The polarization experiments we carried out show that neither of the two characteristic emission bands is polarizable. This result is somewhat unexpected. It is an accepted theory⁴⁰ that excitons in alkali-halide crystals become self-trapped during relaxation. The hole component is located in two neighboring halide ions and forms a quasimolecular V_k center. Electrons recombining radiatively with the V_k centers will give an emission with the electric field parallel or perpendicular to the axis of the V_k center. The excitonic emission from an alkali-halide crystal populated with aligned V_k centers will be polarized. The results of our experiments indicate that either the V_k state was not reached before the electron-hole recombination occurs was reached briefly but not detected with our setup or the orientation is lost during the relaxation process.

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