PHYSICAL REVIEW B VOLUME 15, NUMBER 12 15 JUNE 1977

Luminescence from bound excitons in CsI†

Clayton W. Bates, Jr.
Departments of Materials Science and Engineering and Electrical Engineering,
Stanford University, Stanford, California 94305
Akinola Salau
Department of Applied Physics, Stanford University, Stanford, California 94305

Daniel Leniart
Instrument Division, Varian Associates, Palo Alto, California 94303
(Received 28 May 1976)

The ultraviolet absorption, photoluminescence, and electron-spin resonance (ESR) of pure CsI which had not been exposed to ionizing radiation and which was relatively strain and defect free was studied between room and liquid-helium temperatures. Bulk single crystals were used in the photoluminescence and ESR experiments and both bulk single crystals and thin films 500–2000 Å thick were employed for taking the ultraviolet absorption data. At room temperature before cooling no emissions or ESR signals were observed for any of the samples investigated. As the temperature was lowered to that of liquid nitrogen two emissions with $\lambda_{\max}$ at 420 and 350 nm appear for excitation in the 205–235-nm range, i.e., from the excitonic region to the long-wavelength tail of the fundamental absorption. The 350-nm emission is excited most efficiently in the excitonic region 205–225 nm, whereas the 420-nm emission is more readily produced by excitation in the long-wavelength tail of the fundamental absorption at 235 nm. This general behavior continues down to liquid-helium temperatures. At the temperature of liquid helium (4.2°K) an emission at 2900 Å appears under excitation in the excitonic region and disappears at ~25°K. This emission has been observed by other workers and will not be dealt with here. An interesting effect has been observed when the samples are temperature cycled between room and liquid-nitrogen and lower temperatures. Emissions which were not present at room temperature before cooling appear in the 350–550-nm range depending on the excitation wavelength. It has been found that the intensities of these room-temperature-after-cooling luminescences are approximately 30–40% stronger when the samples are exposed to radiation in the 205–235-nm range when at the lower temperatures before warming back to room temperature, relative to samples which were not similarly exposed. ESR data were taken on pure single crystals of CsI and single crystals of CsI doped with thallium (0.1 mole%) and sodium (0.01 mole%). Experiments were performed on the doped samples, which are known from previous studies to produce stable hole centers at liquid-nitrogen temperatures, to compare with the pure samples which under conditions of high gain hint at the presence of an anisotropic holelike paramagnetic center. At room temperature the pure samples showed no ESR signals. Cooling slowly to about 80°K produced an ESR signal described by magnetic parameters indicating the presence of an F center. The signal is characterized by a g value of 2.003 ± 0.001 with a peak-to-peak linewidth of 100 G and is isotropic in nature. The signal intensity increased as the temperature was lowered to 80°K and changed very little between 80 and 20°K, the maximum amplitude occurring between 60 and 70°K, with the signal intensity remaining isotropic. The signal persists upon warming back to room temperature which correlates quite nicely with the optical data. Effects to correlate the holelike center observed in pure CsI with hole centers observed in CsI(Tl) and CsI(Na) were only moderately successful. Using the theoretical model developed by Bassani and Inchauspe for determining the positions of the α and β bands in CsI we obtain values of 235 ± 5 and 224 ± 2 nm, respectively, for these bands, which coincide with the peaks observed in the excitation spectra for the 350- and 420-nm emissions, further suggesting that the observed emissions are due to the annihilation of excitons bound to negative-ion vacancies (α bands) and excitons bound to F centers (β bands). These observations seem to imply that in pure CsI cooling to liquid-nitrogen and lower temperatures produces traps for both electrons and holes which persist upon warming back to room temperature and that these centers are responsible for the luminescence observed at room temperature after cooling. At low temperatures these traps are probably produced by the thermal-expansion-coefficient mismatch between the crystal (or film), the vacuum grease, and the copper block which constitute the sample holder of the experimental Dewar.

I. INTRODUCTION

A combined study of the optical properties and electron-spin resonance (ESR) of pure CsI from room temperature to liquid-helium temperatures was undertaken to elucidate the fundamental mechanisms involved in the intrinsic luminescence of this material for excitations extending from the long-wavelength tail of the fundamental absorption through the excitonic region, i.e., 205–235 nm. This work was done because relatively few studies have been made of alkali halide crystals with the CsCl structure. CsI is one of the most sensitive detectors of ultraviolet radiation and when activated with sodium it is an extremely efficient x-ray scintillator.[1-4]

Previous attempts to understand centers responsible for luminescence observed in alkali halide crystals involved doping the crystals with monovalent or divalent cationic impurities like Na^+, Tl^+, Li^+, Sr^{++}, and Mn^{++}, electron traps being introduced in the case of monovalent impurities and cation vacancies for divalent impurity doping.[5-8] In other situations crystals were irradiated with high-energy particles such as x-rays or γ rays to create color centers.[9-11] Recent studies showed that energies of the orders of 5–10 eV were enough to create color centers in alkali halide crystals.[12,13]

The intrinsic luminescence which occurs at liquid-nitrogen temperature (LNT) in alkali halide crystals has been attributed by Kabler and also Murray and Keller[14] to the recombination of an electron and V_k center (self-trapped hole), this configuration being denoted by $(V_k+e)^*$. This model has been used extensively to explain the intrinsic luminescence excited with either ultraviolet light or with x rays at low temperatures. There is limited literature on the optical properties of pure CsI which has not been exposed to ionizing radiation and which is relatively strain and defect free.[15,16] Most of the existing data on the optical properties of strain-free CsI are on ultraviolet absorption spectra.[17] The results of Lamatsch *et al.*[15] on ultraviolet absorption spectra of thin films of relatively strain-free CsI agree with our results.

Some authors have studied the optical properties of deformed bulk single crystals of unactivated CsI.[18-21] One of these authors[18] observed an emission that peaked within the range 415–430 nm, the so-called blue luminescence at room temperature before cooling in their deformed specimens (that is specimens in which structural lattice defects or strain have been introduced). At LNT, these authors observed besides the blue luminescence, an ultraviolet luminescence peaking within the range 330–360 nm for both excitonic and fundamental absorption-edge excitations.

The present work deals with relatively strain- and defect-free pure CsI. We have combined optical techniques with electron-spin resonance to investigate the luminescent phenomena in pure CsI. The optical techniques through absorption, emission and excitation spectra gives information on the electronic transitions occurring in the material and the ESR reveals the nature of the trapping sites, which from previous studies we expect to be paramagnetic.[9] It was felt that correlating the optical spectra with ESR would more firmly establish the authenticity of our interpretations.

II. EXPERIMENTAL

In this paper the luminescence of CsI will be described in terms of optical studies consisting of absorption, emission and excitation spectra, and ESR. The measurements were performed from room to liquid-helium temperatures. The methods used to measure them are described in the following appropriate paragraphs.

A. Optical studies

1. Optical absorption

Evaporated thin films of pure CsI were obtained using suprapure powders purchased from the Merck Co. while the bulk single crystals were grown by the Harshaw Chemical Co. The sodium content of the Harshaw sample was less than one part per million. These bulk single crystals measured $1.27\times1.27\times0.2$ cm^3 in size. These crystals were mounted on a copper sample mounting block with silicone grease in the experimental Dewar.

A vapor-deposition technique was used to evaporate our films.[22] These films were evaporated on room-temperature (RT) (300 °K) or hot (400 °K) suprasil quartz II substrates $1.27\times1.27\times0.1$ cm^3 in size and then annealed at this temperature for a period of 12 h and slowly cooled to RT at a rate of roughly 8.3 °K/h to produce relatively strain- and defect-free films. More rapid cooling produced strains in the films which then luminesced at RT before cooling.[23] Heating was provided by a stainless-steel block with heaters and a chromealumel thermocouple embedded in it upon which the substrates were mounted. The thickness of the films deposited were measured by a Sloan DTM gauge connected to a quartz sensor head in the vacuum chamber.

The vacuum system consisted of a standard Varian Associates FC12-E high-vacuum system containing two vacsorbs, titanium sublimation pump, 200-liter/sec vacion pump and a cryopump. This system provided fast pumping speed and extremely low contamination which is more difficult to achieve with oil diffusion pumps. The pressure during evaporation was typically about 10^{-9} Torr. The films used in the absorption studies were 500–2000 Å thick. The thin-film data presented were taken from films 600 Å thick.

After the films were prepared in vacuum, the system was let down to nitrogen and the samples were transferred to the experimental Dewar while continuously blowing dry nitrogen gas on them. The Dewar was a 024/7M variable temperature cryogenic system made by Andonian Cryogenics, Inc. A Cary 14 spectrophotometer was used to measure the absorption spectra of thin films and the bulk single crystals which had 100 faces perpendicular to the radiation in the Cary 14.

2. *Emission and excitation*

To measure the excitation and emission spectra, a conventional arrangement as shown in Fig. 1 was used. The light source was a Bausch and Lomb deuterium lamp which had a fairly flat spectrum from 2000 to 4000 Å without any sharp lines. The light went through a grating monochromator which had a small driving motor to provide steady scanning speed, and then through a mechanical light chopper. The chopped monochromatic light was incident upon the large face of the samples (the 100 face in the case of single crystals) in the Dewar. The emission was measured at right angles to the exciting light in order to avoid the interference from the transmitted and reflected light. Passing through another grating monochromator, the emission was detected by an RCA 8645 photomultiplier tube with an S-20 spectral response. The detected signal was fed into a lock-in amplifier, which picked up the reference frequency from the chopper, and then recorded by a strip-chart recorder. Measurements were made first at room temperature and then the sample was cooled to liquid-helium temperatures in a continuous fashion and then warmed slowly back to room temperature. Data was taken both during cooling and warming back to room temperature.

B. Electron-spin-resonance studies

The samples used for ESR studies were single crystals all having a rectangular shape of dimensions 15×4 mm^2 and a thickness of 2 mm. The crystals were purchased from the Harshaw Chemical Co. with the pure CsI having an impurity content of <2 ppm or roughly 0.001 mole%, CsI(Na) of 6ppm or 0.01 mole% and CsI(Tl) of 21 ppm or approximately 0.1 mole%. The crystals were attached to a quartz sample holder with Duco cement and rotated about the long axis with a goniometer such that the 100 crystallographic direction could be oriented parallel and perpendicular to the dc magnetic field H_0. The experimental apparatus consisting of a standard Varian E-112 ESR spectrometer with a standard E-231 multipurpose cavity operating in the TE$_{102}$ mode was used along with a standard Dewar insert and variable temperature unit (E-257) operating between 80 and 573 °K. All spectra were recorded using a field modulation frequency of 100 kHz and a peak-to-peak field modulation amplitude of 20 G. Although the incident microwave power on the cavity was varied, generally, experiments were carried out at incident powers of 200 mW for purposes of sensitivity. Field scans of 1 to 4 kG centered about $g = 2$ (~ 3.3 kG) were chosen to present the data in the most convenient manner.

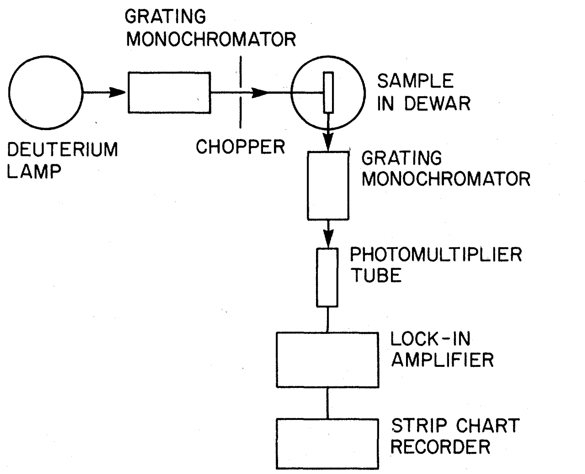

FIG. 1. Experimental setup for emission and excitation measurements.

ESR experiments at 20 °K were done with a helium flow system employing a home-built transfer tube, a silvered extension Dewar, and a standard E-231 cavity Dewar insert. One end of the transfer tube was immersed in a 25-liter He Dewar while an extension Dewar was attached to the other end and to the standard Dewar with common pinch clamps to glass ball and joint sockets. The total distance from the He Dewar to the ESR cavity was about 1 m. The temperature at the sample was controlled by regulating the flow rate of He gas over the sample—He dissipated at a rate of about 1 liter/h was sufficient to maintain a sample temperature of ~20 °K. The flow rate was controlled by the amount of power dissipated in a 2-W resistor attached to the immersed end of the transfer tube, the current through the resistor being controlled with a standard 0–20-V, 0–1.5-A Harrison 6201A dc power supply.

Optical irradiation of the sample was done with a Bausch and Lomb high-pressure Hg vapor lamp and attachable monochromator. The incident light passed through the optical grid of the standard microwave cavity (50% transmission) through a suprasil quartz Dewar insert and onto the sample. In nearly all cases, sample irradiation was done at 217 and 235 nm, the first exciton absorption band and the absorption edge, respectively.

III. RESULTS

A. Optical absorption

Measurements were performed on both thin films and bulk single crystals, the thin films being used for measurements between room and liquid-nitrogen temperatures while the bulk crystals were employed in the 150 °K to liquid-helium tempera-

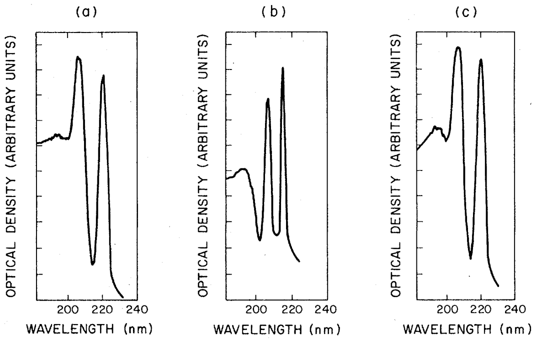

FIG. 2. Absorption spectra of thin film at (a) RT before cooling; (b) LNT; and (c) RT after cooling.

ture range.

The ultraviolet absorption spectra of the thin films (600 Å) of pure CsI are shown in Fig. 2. At RT (before and after cooling) absorption peaks are observed at 220 nm (1st exciton band) and 205 nm. These peaks sharpened, with the 220-nm band shifting to 215 nm at LNT as shown in Fig. 2. The shift of the first exciton absorption band (220 nm) at RT to 215 nm at LNT is probably due to strain induced by cooling. This effect has been noted by Lynch and Brothers.[16] The bulk single crystals which were $\frac{1}{2}$ in. $\times \frac{1}{2}$ in. $\times$ 2 mm and had the (100) face perpendicular to the radiation in the Cary 14, were used to reveal any structure occurring in the long-wavelength tail of the fundamental absorption. The absorption spectra for these crystals in this region are shown in Fig. 3. for temperatures of 120, 80, 60 °K, and liquid-He temperature (LHeT). At 120 °K absorption peaks appear at 225 and 245 nm. The position and relative intensity of the 225-nm peak does not appear to change much with temperature. The peak at 245 nm at 120 °K shifts to 240 nm at 80 °K, 238 nm at 60 °K, and 237 nm at LHeT, the relative intensity almost doubling in this sequence.

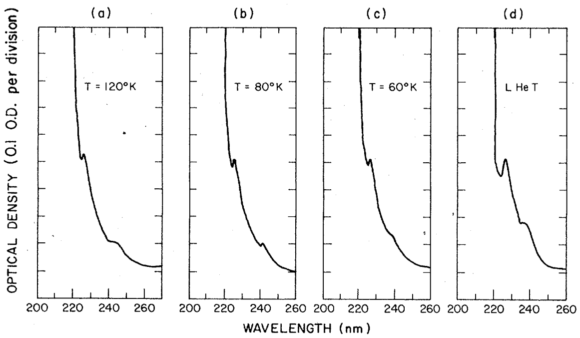

FIG. 3. Absorption spectra of bulk single crystal at (a) 120 °K; (b) 80 °K; (c) 60 °K; and (d) LHeT.

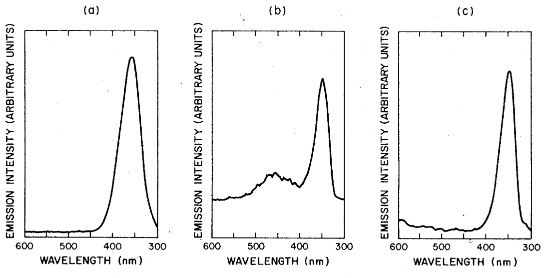

FIG. 4. Emission spectra of thin film of CsI at (a) LNT for $\lambda_{ex} = 215$ nm; (b) LNT for $\lambda_{ex} = 235$ nm; (c) RT after coding for $\lambda_{ex} = 235$ nm.

B. Emission and excitation

Because of temperature cycling we have for convenience divided our results into data between room RT and LNT and RT and LHeT.

1. *Thin films*

Figure 4 shows the emission spectra which were measured for thin (600 Å) films of pure CsI. As in prior studies,[15] emission was not observed at room temperature before cooling for excitation at the absorption edge or the excitonic region. Excitation in the excitonic region at LNT, however, produced emission that peaked at 350 nm while excitation in the fundamental absorption edge produced a weak luminescence at 430 nm in addition to that at 350 nm. When the sample was warmed to RT, the crystal exhibited a room temperature after cooling luminescence which peaked at 350 nm.

Figure 5 shows excitation spectra for thin films

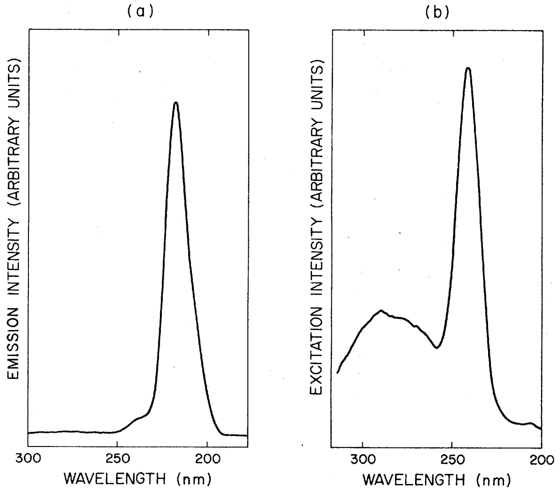

FIG. 5. Excitation spectra of thin film of CsI at (a) LNT for emission at 350 nm; (b) RT after-coding for emission at 350 nm.

for ultraviolet emission at 350 nm at LNT and RT after cooling. At LNT, the excitation spectra has a strong peak at 217 nm and a smaller one at 235 nm while the RT after-cooling spectrum has a large peak at 235 nm and a broader one centered at 280 nm.

2. *Bulk single crystals*

The bulk single crystals of pure CsI exhibited no emission at RT before cooling but at LNT [Fig. 6(a)] gave rise to both the ultraviolet (350 nm) and blue (420–430 nm) emissions for excitonic and fundamental absorption edge excitations, respectively. RT after-cooling measurements showed emission that peaked at 470 and 540 nm for absorption-edge (235 nm) excitation, as shown in Fig. 6(b). Excitation spectra [Fig. 7(a)] of the uv emission at 350 nm peaked at 220 nm with a relatively small contribution at 235 nm while the blue emission (420–430 nm) has an excitation peak at 240–250 nm on the long-wavelength tail of the fundamental absorption. Figure 7(b) shows the RT after-cooling excitation spectra for emission at 470 and 540 nm, both having an excitation peak at roughly 237 nm.

The absence of luminescence at RT before cooling for excitation either in the excitonic region or the fundamental absorption edge does not agree with Morgenshtern's results[19] who observed emission from his nominally pure CsI samples. From our observations this disagreement might be attributed to the presence in his crystals of trace impurities whose importance as a source of luminescence was not appreciated at the time. Other authors[18,20,21] observed RT before-cooling luminescence in pure CsI but only after they had either been plastically deformed or quenched to RT from high temperatures.

The ultraviolet luminescence at 350 nm observed at LNT in both thin films and bulk single crystals of pure CsI for excitonic excitations is in agreement with other prior studies.[15] That the corresponding excitation spectra peaks at 217–220 nm in the excitonic region (with humps at 235–237 nm) supports our contention that this luminescence is due to electron-hole radiative recombinations at sites created by cooling and exposure to nonionizing ultraviolet light. Absorption-edge excitation (234 nm) at LNT gives strong luminescence at 425 nm for the bulk single crystals and both a weak luminescence at 430 nm and strong one at 350 nm for the thin films. The excitation spectra of the blue luminescence (425–430 nm) peaks at 237 nm.

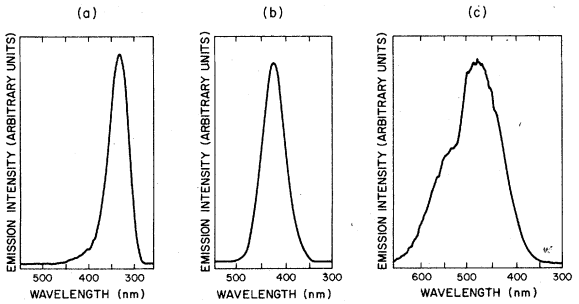

FIG. 6. Emission spectra of bulk single crystal of CsI at (a) LNT for excitation at 215 nm; (b) LNT for excitation at 235 nm; (c) RT after-coding for excitation at 235 nm.

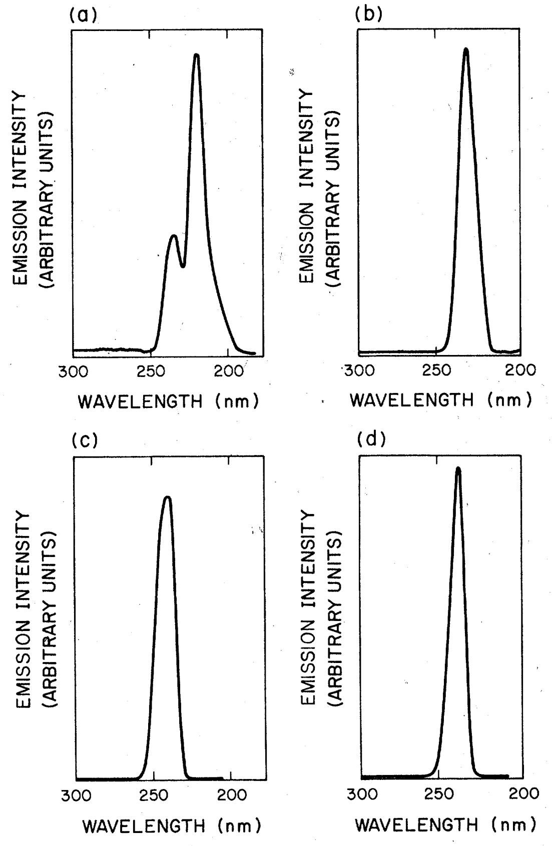

FIG. 7. Excitation spectra of bulk single crystal of CsI at (a) LNT for emission at 350 nm; (b) LNT for emission at 425 nm; (c) RT after coding for emission at 470 nm; (d) RT after coding for emission at 540 nm.

When these samples warmed from LNT to RT, they exhibited luminescence for absorption-edge excitation which was not observed at RT before cooling. This RT after-cooling luminescence for the thin films might be tentatively explained as being from radiative electron-hole recombination at sites created by (i) cooling or temperature cycling, and (ii) exposure to nonionizing uv radiation at LNT. Figure 8 shows that the intensity of the RT after-cooling luminescence at 350 nm for an unirradiated sample at LNT is less than that of a sample which had been exposed to nonionizing uv radiation at LNT. This suggests that the center responsible for the RT after-cooling luminescence is created by temperature cycling (cooling) and apparently further enhanced by irradiation with nonionizing ultraviolet light at LNT. As one explanation, the disappearance of RT luminescence from thin films through annealing might indicate that the center which is responsible for the RT after-cooling luminescence is associated with structural lattice defects (perhaps of the vacancy type) in the crystals.

Using the model developed by Bassani and Inchauspe,[24] we calculated the positions of the α and β bands in CsI to be, respectively, located at 235 ± 5 and 224 ± 2 nm. Pauling's theoretical values of ionic polarizability[25] and the position of the F band given by Lynch *et al.*[26] have been used.

The ratio of the position of the β band relative to the first exciton absorption band to that of the α band is in agreement with those calculated by Bassani and Inchauspe for some alkali halides crystals.[24] In plastically deformed CsI(Na), the supposed α and β bands are well resolved.[23]

Therefore, as another explanation, the peaking of the excitation spectra at RT after cooling of the ultraviolet and both the blue and yellow luminescence at 235 nm (the position of the α band in CsI) and a small contribution from the 280-nm band suggests that the RT after-cooling luminescence observed in CsI is probably due to radiative recombinations of excitons trapped at halogen-ion vacancies and electron excess centers which were produced by cooling and exposure to nonionizing uv radiation at LNT.

The following discussion concerns measurements between LNT and LHeT and were taken exclusively on bulk single crystals.

The low-temperature luminescence of relatively strain- or defect-free and pure CsI is excitable in both the excitonic and fundamental absorption bands. Excitations in the excitonic region give rise to three emission bands at 300, 350, and 430 nm, respectively, at temperatures below 25 °K the 300-nm band presumably being that measured by Lamatsch *et al.*[15] At 25 °K and above, the 300- and the 430-nm emission bands were unmeasurable for excitonic excitations but the 350-nm emission intensity correspondingly increases and stays constant up to 77 °K (LNT) after which at 90 °K the intensity drops considerably to about (10–15)% of its value at LNT. At about 150 °K and above this 350-nm emission band was unmeasurable for excitonic excitation. The evolution of the emission intensities of the 300, 350, and 430 nm for excitonic excitations as a function of temperature is shown in Fig. 9(a). Figure 9(b) gives the excitation spectra for these emissions at 10 °K.

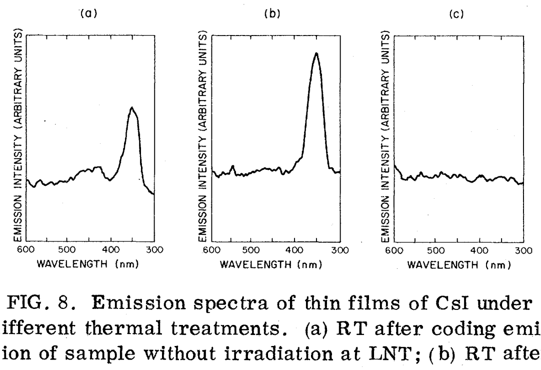

FIG. 8. Emission spectra of thin films of CsI under different thermal treatments. (a) RT after coding emission of sample without irradiation at LNT; (b) RT after-coding emission of sample with irradiation at LNT; (c) RT before-coding emission of sample which previously showed RT after-coding luminescence and then annealed again. All excitations at 235 nm.

Figures 10(a) and 10(b) shows the evolution of the emission spectra of a bulk single crystal of CsI as a function of temperature for excitations at the α band (235 nm) and the β band (225 nm). Between 20 and 77 °K, the emission intensities of the 430- and 320-nm bands are relatively constant for β-band excitations as shown in Fig. 10(b). For α-band excitation, within this temperature

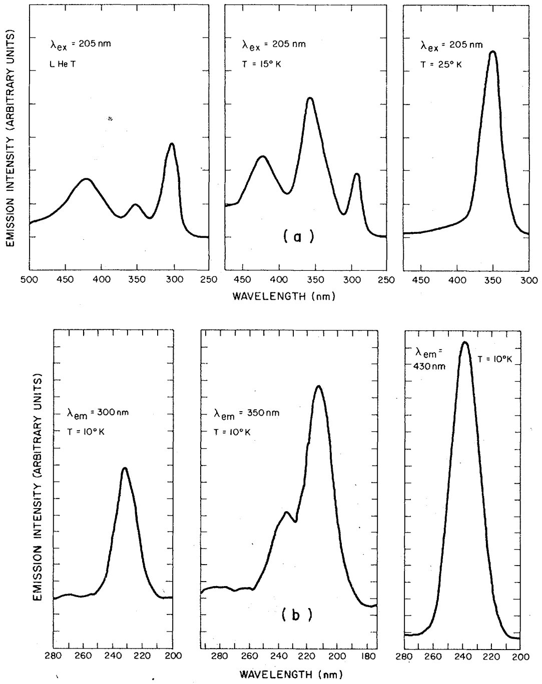

FIG. 9. Emission and excitation spectra of bulk single crystal of CsI. (a) Emission spectra of 300-, 350-, and 430-nm emissions for excitonic excitations as a function of temperature; (b) excitation spectra for these emissions at 10 °K.

range, the emission intensity of the 430-nm emission band is constant but though the 320-nm emission band has constant emission intensity between 60 °K and 77 °K and a weaker emission intensity at 35 °K, it disappears at 20 °K when a new band appears at 380 nm. It is interesting to note that at 90 °K, the 320-nm band disappears for excitations in either the α or β band and the intensity of the 430 nm decreases. Figure 10(c) gives the excitation spectra at 20 °K.

C. Electron-spin resonance

1. Pure CsI

Since the optical studies indicate that the basis for creating exciton trapping sites is primarily through the cycling of the temperature, it was decided to investigate the actual trapping sites themselves by combining optical techniques with electron-spin resonance. If the trapping sites are, indeed, paramagnetic,[9] then it should be possible to determine some of the important magnetic parameters and perhaps more fully characterize the sites themselves. In addition, one should, in principle, be able to observe any effect that the incident irradiation has with respect to a particular trapping site.

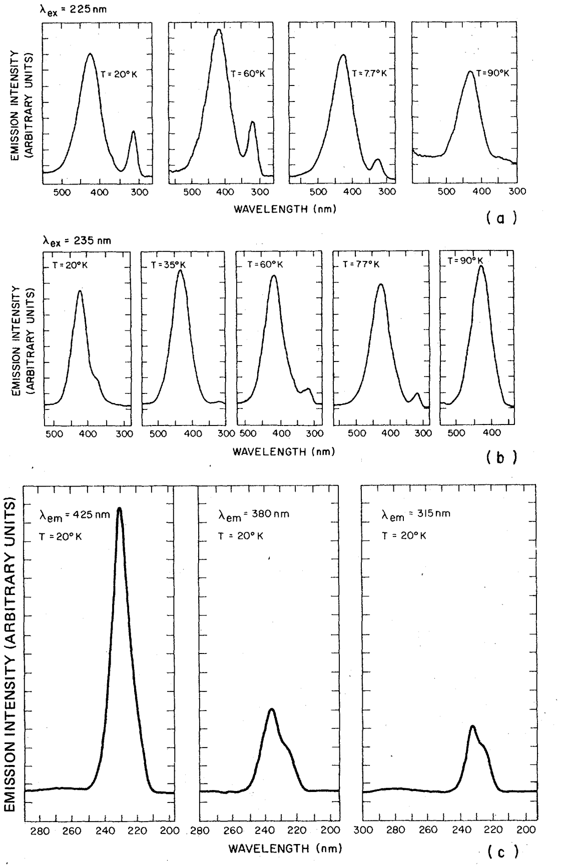

FIG. 10. Emission and excitation spectra of bulk single crystals of CsI as a function of temperature. (a) Emission spectra for α-band excitation; (b) emission spectra for β-band excitation; (c) excitation spectra at 20 °K.

Immediately after receipt, the pure Harshaw crystals were placed in the spectrometer and weak ESR signals were observed at room temperature. Upon annealing at 520 °K for a 4–5-h period, slowing returning the sample to room temperature in steps of 10 deg every 20 min, and recording the ESR spectra under the same experimental conditions, all ESR signals disappeared. Signals from the unannealed crystals were tentatively assigned to defects produced by the cutting, grinding, and polishing of the pure material by the supplier. As standard practice, it is suggested that all pure crystals be annealed, as described above, before any ESR studies are done to eliminate any complicating ESR structure.

As the pure crystal was slowly cooled to 80 °K, an ESR signal appeared described by magnetic parameters indicating the presence of a defect believed to be that of an *F* center. The signal is characterized by a *g* value of 2.003 ± 0.001 and a peak-to-peak linewidth of approximately 100 G. The signal intensity increased (the line shape remained unchanged hence the peak-to-peak amplitude increased) as the temperature was lowered to 80 °K and changed very little between 80 °K and 20 °K (due presumably to saturation)—the maximum amplitude occurring at ~ 60–70 °K. The line shape was essentially Gaussian and at 80 °K showed initial saturation above roughly 40 mW incident power upon the cavity and seemed to retain its initial line shape when saturated up to 200 mW. This saturation behavior is usually characteristic of lines that are inhomogeneously broadened.

Upon warming of the sample from 80 °K to room temperature the ESR signal continues to persist. (See Fig. 11.) Only annealing at evaluated temperatures will successfully bleach the pure CsI crystal. Regardless of the number of bleachings and coolings the pattern is as follows: RT before cooling—no ESR signals. 80 °K—ESR signals—*F* centers. RT after cooling—ESR signals—*F* centers.

There appears to be no hyperfine structure on the ESR line attributed to the *F* center and no obvious asymmetry of the *F*-center line itself.

Under conditions of rather high gain there is an indication of a wealth of ESR lines down in amplitude by 1–2 orders of magnitude relative to the *F*-center signal and which appears to be anisotropic in nature. Apparently, the responsible electrons are in rather shallow traps since warming to room temperature is sufficient for bleach-

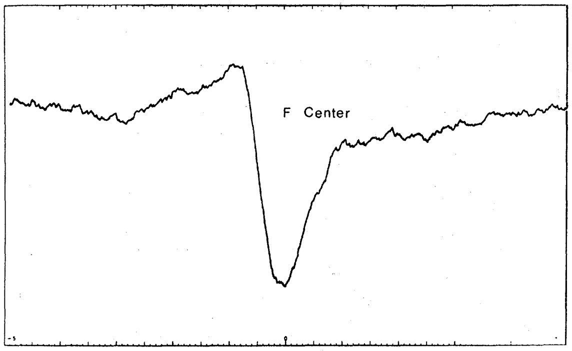

FIG. 11. RT after-cooling ESR signal of pure CsI. Scan rate, 1 kG; $H_0 = 3230$ G; modulation amplitude, 20 G; microwave power, 100 kHz; $\nu_0 = 9.15$ GHz; response time, 1 sec; microwave power, 200 mW; temperature, room (after cooling); receiver gain, 3.2×10^4.

ing. However, we hesitate to make any further statement with respect to their origin with the S/N presently obtainable. As the pure CsI crystal is cooled in the presence of optical irradiation at both 217 and 235 nm the amplitude of the ESR signal is relatively light insensitive—perhaps a 5% increase in the ESR signal is observed—and remains unchanged at a variety of other wavelengths and optical intensities.

2. *Optical-grade* CsI(Tl)

Upon annealing the optical-grade thallium doped (0.1 mole %) CsI crystal a large ESR signal was recorded at both 540 and 297 °K. At 540 °K a rather symmetric ESR line was observed having a peak-to-peak linewidth of approximately 100 G and a rather large g value of 2.06 ± 0.002. A narrow ESR line ($\delta = 20$ G) appeared at slightly higher field characterized by a g value of 2.00 ± 0.02 with a hint of structure. Upon cooling to room temperature, the latter line remained unchanged in position and decreased in amplitude by about a factor of 2–3. All indications of structure disappeared.

On the other hand, the low-field ESR linewidth remained constant, but the spectral center shifted downfield by roughly 100 G giving a room-temperature g value of 2.090 ± 0.002. In addition to the field shift, structure appeared on the shoulders of the line while the amplitude decreased to roughly one-half its value at the higher temperature. The line shape at this temperature was independent of crystal rotation. This sequence is shown in Fig. 12 and is given in Table I.

Further cooling of the CsI(Tl) crystal to 80 °K gives rise to a large ESR signal that can be easily decomposed into two lines—one is the "low-field" ESR line observable at higher temperatures having

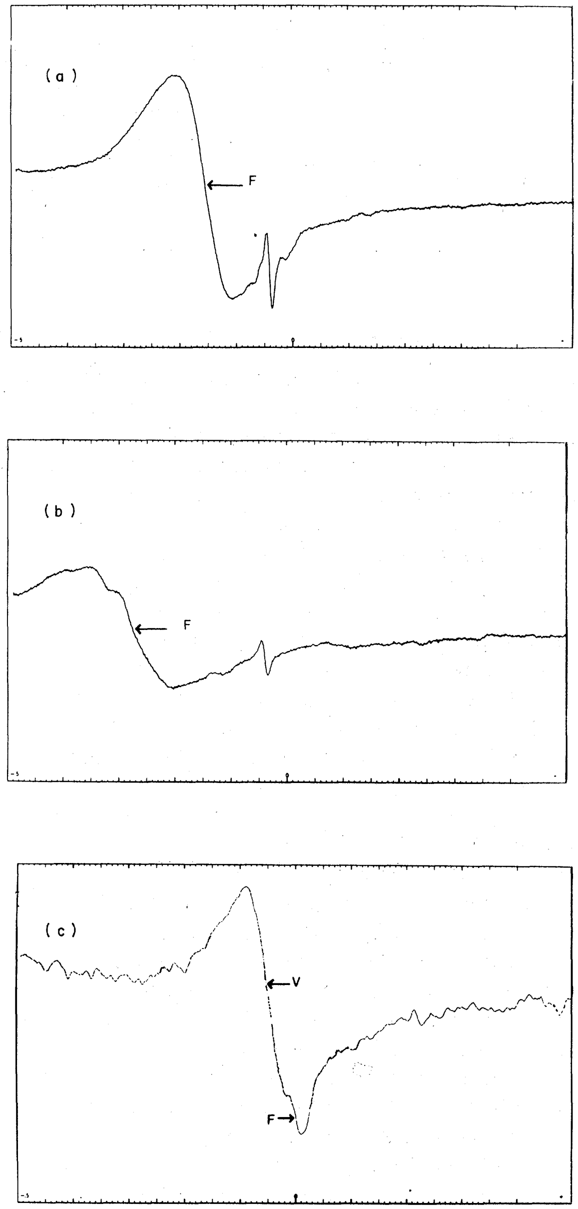

FIG. 12. ESR spectra of CsI(Tl) as a function of temperature. (a) Tl-doped CsI annealed at 260 °C for 10 h Scan range = 1 kG; $H_0 = 3321$ G; modulation amplitude-20 G; modulation frequency = 100 kHz; $\nu_0 = 9.15$ GHz; response time = 0.250 sec; microwave power = 200 mW. temperature = 260 °C; receiver gain = 6.3×10^3. (b) Tl-doped CsI annealed for 10 h at 260 °C and brought to room temperature over a 5-h period. Scan range = 1 kG; $H_0 = 3321$ G; modulation amplitude = 20 G; modulation frequency = 100 kHz; $\nu_0 = 9.15$ GHz; response time = 0.250 sec; microwave power = 200 mW; temperature = room; receiver gain = 6.3×10^3. (c) Tl-doped CsI at − 175 °C. Scan range = 4 kG; $H_0 = 3200$; modulation amplitude = 10 G; modulation frequency = 100 kHz; $\nu_0 = 9.15$ GHz; response time = 1 sec; microwave power = 100 mW; temperature = 175 °C, receiver gain = 1.6×10^4.

TABLE I. Experimental sequence of events in recording the ESR spectra of CsI(Tl) at three difference temperatures.

	540 °K Structure	 g value	 δ (p-p)	297 °K Structure	 g value	 δ (p-p)
Low-field line	No	2.06	100	Yes	2.09	100
High-field line	Yes	2.00	20	No	2.00	20

	80 °K Structure	 g value	 δ (p-p)
Broad line	Yes	2.205	$\sim$1 kG
Low-field line	Yes	2.042	100 G
High-field line	Disappeared		

a $\delta = 100$ G and a g value of 2.042 ± 0.002, while the second is a new ESR center having a g value of 2.205 ± 0.004 and a peak-to-peak linewidth of ~ 1 kG. The new line shape is dependent upon crystal orientation and on temperature and has an overall intensity that is much greater than that of the $\delta = 100$-G ESR line. Tentatively, an assignment of the $g = 2.04 \pm 0.002$, $\delta = 100$ G corresponding to that of an F center and the $g = 2.205 \pm 0.002$, $\delta \sim 1$ kG, anisotropic, broad ESR line to that of a V center (self-trapped hole) is made (vide infra). [See Fig. 12(c).] Upon warming back to room temperature, the ESR line corresponding to the V center is significantly broadened, the linewidth increases by more than a factor of three and the signal intensity drops by something greater than an order of magnitude. The ESR line corresponding to the F center persists in RT after cooling. As in the case of the pure crystal irradiation of the thallium-doped has little effect on the ESR signal.

To support the contention that the X band observed in the optical spectrum was specifically related to a V_k center it was thought that perhaps this center might be observable in the ESR spectrum. Heretofore V_k centers have been studied extensively in alkali halide structures and in particular has been observed in CsI(Tl) to give an $11 = 2I + 1$ line ESR spectrum arising from the molecular ion I_2^- (nuclear spin of iodine: $I = \frac{1}{2}S$). However, to our knowledge, all V_k centers found in the literature have been produced in the presence of *ionizing* (x ray) irradiation. It was hoped to observe the presence of such centers upon cooling the sample to 20 °K in the presence of *nonionizing* irradiation (uv at ~ 5 eV). Experimental ESR results do not show the presence of an eleven line V_k center spectrum at the necessary levels of concentration [$2 \times 10^{10}\ \delta x(2I+1)$ spins in the cavity: 2×10^{14}] spins in the volume (~ 0.1 cm^3) of CsI(Tl) crystal used in the experiment.[27]

3. Optical-grade CsI(Na)

The sodium-doped CsI crystal (0.01 mole%) behave in much the same way as the thallium-doped signal in that indications of both F and V centers appeared upon cooling the sample to 80 °K. Best signal resolution occurred at ~ 173 °K. However, unlike the Tl-doped material, this sample did bleach upon being warmed to 473 °K and then cooled to room temperature. Details of the work on this system will be published at a later date.

D. Additional irradiation studies

Since the technique of irradiating pure CsI samples during cooling produced a small increase (5%) of the ESR signal during the time of irradiation which was several minutes at best, it was decided to irradiate a sample for several hours with ultraviolet light at low temperatures and then observe the ESR signal. The results are shown in Fig. 13 for a pure sample of CsI which had been irradiated by means of a high-pressure Hg vapor lamp for 6 h at a temperature of about 6 °K. The ESR signal intensity has increased by almost an order of magnitude over the previous one for pure CsI. This result appears to confirm the proposition that not only can F centers be produced by ultraviolet radiation,[12] but also the wealth of orientation-dependent ESR structure indicates the presence of an anisotropic V center. It is still not possible at this time to analyze the anisotropic ESR spectrum and to assign a structural model designating the particular V center involved.

E. Additional absorption studies

The tentative assignment of the ESR signal as being due to that of the F center was based on three supporting pieces of data: (a) the ESR signal is isotropic; (b) has a g value close to that of the free electron; (c) and a calculation of the position of the α and β bands in CsI shows them to be located at the experimentally observed peaks at 235 and 225 nm on the long-wavelength tail of the fundamental absorption.

To reinforce this contention we looked for an absorption in the spectral region where others had found absorption which they attributed to the

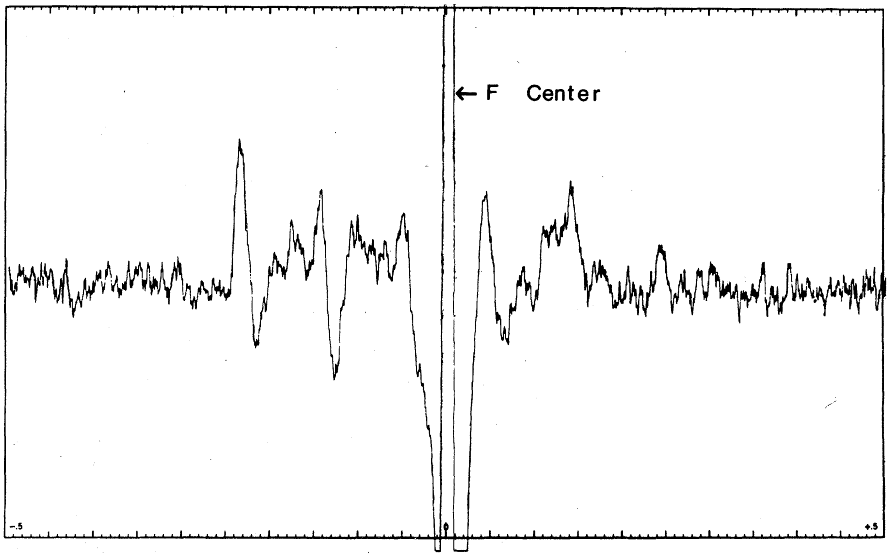

FIG. 13. Pure CsI irradiated at 6 °K with Hg lamp for 6 h and stored at liquid-nitrogen temperature for three days. Second-derivative ESR spectrum. Scan range = 1 kG, H_0 = 3588, modulation amplitude = 32 G, at 100 kHz modulation frequency and 20 G at 35 Hz, modulation freqeuncy; $\nu_0 = 9.58$ GHz; response time = 3 sec; microwave power = 80 mW; temperature = ~ 10 °K; receiver gain = 2.5×10^2 at 100kHz and 2.5×10^2 at 35 Hz.

presence of the F center.[28-31] In these experiments we had to use a special slidewire in the Cary 14R spectrophotometer which allowed a range of optical density of 0–0.2. to be measured over 10 in. of chart paper. In these measurements bulk single crystals of pure CsI were used. At room temperature before cooling to LNT no absorptions were observed from about 3000 Å to 2.6 μm. At LNT absorptions appear at 840 nm and 1.28μm. At room temperature after cooling these signals persist but slightly reduced in amplitude. If one bleaches the crystal with 840-nm light for 12 h, the 840-nm absorption decreases while the 1.28-μm absorption increases. The area under the 840-nm absorption changes very little between LNT and RT after cooling. These results are given in Fig. 14. These observations would lead one to tentatively assign the 840-nm absorption to the F band and the 1.28-μm absorption to the M band except that previous studies[28-31] have indicated that the F band in CsI is located at 740 nm and the M band at 1.18 μm. These are both shifted down in wavelength from our values by 100 nm a fairly large shift. We have no explanation for this at this time. However, the fact that the temperature cycling behavior of these absorptions follows that of the ESR signals leads one to associate this absorption with the paramagnetic species produced by the temperature cycling. The assignment of the paramagnetic species to the F center is thus still tentative.

IV. DISCUSSION

Cooling and exposing CsI which is relatively pure and strain and defect free to nonionizing uv radiation at low temperatures, suggests from absorption studies and reinforced by theoretical calculations the creation of halogenion vacancies and F centers which act as recombination sites or traps for free holes and electrons or mobile excitons. These vacancies and F centers appear to be created by the strain induced during cooling by the thermal-expansion mismatch between the crystal, the vacuum grease, and the copper block in the Dewar and enhanced by exposing the sample to nonionizing uv radiation. Thus the RT after-cooling luminescence can tentatively be associated with vacancies (traps) or other lattice imperfections created by the motion and clustering of dislocations which exist in the crystal as a result of thermal contraction of the crystal during cooling. That the cooling acts as a plastic deformation can be explained as follows. It has been shown that the minimum external stress required to move a dislocation in simple cubic crystals is very small (~ 10^5 dyn/cm^2.[25] This is three orders of magniture less than the critical shear stress of 10^8 dyn/cm^2 induced by cooling in CsI.[25,32] Also it should be noted that the elastic limit observed in CsI is of the order of 10^7 dyn/cm^2 one order of magnitude less that that induced by cooling. Consequently we are

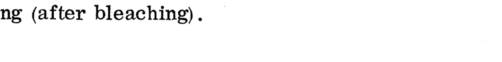

FIG. 14. Absorption spectra of F and M bands in pure CsI. (a) At LNT (before bleaching); (b) at RT after cooling (after bleaching).

led to the conclusion that cooling produces plastic deformation in CsI because (i) the stress produced by cooling as a result of thermal contractions makes the dislocation highly mobile which in turn is responsible for slip that produces, in many crystals, plastic deformation; (ii) cooling-induced stress exceeds the measured elastic limit; and (iii) RT after-cooling photoluminescence measurements persists even after several days, though the peak position of the excitation spectrum shifts to longer wavelengths (250 nm) after about 2 weeks. Therefore, dislocation motion and clustering as a result of thermal contraction of the crystal due to cooling produces vacancies and other lattice imperfections that act as traps for electrons and holes or mobile excitons. However, it should be noted that the concentration of traps thus produced by cooling (without irradiation at low temperature) is very small[33] ($\sim 10^{15}\mathrm{cm}^{-3}$) and we are able to detect absorption bands in the infrared region in our crystal only at very high sensitivity. The absorption bands are located at 840 and 1280 nm which are shifted by 100 nm from the normal F and M bands in CsI. The location of F and M bands 100 nm higher in wavelength than that previously observed does appear at this time to make the assignment of an F center somewhat tentative in spite of the previous supporting data.

ESR studies on both pure and doped CsI crystals suggest the presence of an F center, i.e., an electron occupying an anionic vacancy, produced by the inherent stress or strains that permeate the sample upon cooling to 80 °K. Experimental evidence showing the presence of (i) a small g-shift from the free electron value of 2.0023; (ii) a Gaussian line shape that saturate inhomogeneously; (iii) a peak-to-peak linewidth of ~100 G, suggests the assignment as that of an F center arising from crystal stress or strain upon cooling. Irradiation of pure CsI at both the fundamental absorption edge (235 nm) and 217 nm show photoluminescence when monitoring the optical-absorption emission and excitation spectra. This irradiation also enhances the ESR signal when done for long periods of time (6 h). These experiments suggest that the trapping sites (F centers) are produced by the cooling of the crystal only and that the effect of the light is to excitonically populate the trapping sites. Upon warming, the deep traps continue to be stable allowing radiative exciton recombination with various crystal defects possibly leading to the observed luminescence.

Another possible explanation is that the center we are observing is the F' center, i.e., two electrons trapped at a negative ion vacancy. Intrinsic optical properties of the F' center have not been studied too extensively. A notable exception is the work of Lynch and Brothers[34] who actually measured the location of the F' band in additively colored CsI. Their work showed the existence of a broad band of complex structure extending from 2.25 μm in the infrared to 340 nm in the ultraviolet. There is a well-resolved peak at 827 nm and a hump at 1.1 μm which agrees reasonably well with the bands we observed in our plastically deformed CsI crystals.

Our data both optical and ESR are consistent with such an interpretation. We would expect a broader ESR line with the g value closer to the free-electron value relative to the F center as normally observed. This is supported by our ESR data. However, to the best of our knowledge no ESR studies have been done on F' centers. We would expect the absorption of the F' center to occur at a longer wavelength relative to the F center with a corresponding longer wavelength for an excited state, i.e., the M' band relative to the M band. This could easily explain the 100-nm shifts that we observed.

A second type of center was found in the TI-doped material, and to a lesser extent in the sodium-doped material, which was anisotropic in nature and exhibited a rather broad spectral width of the order of a kilogauss. Cooling the doped CsI crystal can cause a variety of defects and, in particular, a variety of V centers. For example, Kanzig[35] describes a self trapped hole, a hole trapped by a cation vacancy, an unpaired electron located on three halogen atoms, or formation of a molecule ion by an interstitial halogen atom. The tentative assignment of this as a V center seems consistent with experimental data and substantiates the observed luminescence behavior by providing a radiative e^--hole recombination mechanism at sites created by the temperature cycling. Since the V centers are anistropic in nature interesting optical data is likely to be obtained using polarized incident radiation and/or observing polarized luminescence. Experiments of this kind are presently underway.

In conclusion, it appears that upon cooling CsI to low temperatures plastic deformation occurs which produces paramagnetic centers. These centers may be F or F' centers or both and V centers. Taken together we have excitons which radiatively recombine to give rise to the observed luminescence.

ACKNOWLEDGMENTS

The authors would like to express their appreciation to Dr. I. Schneider, Professor W. A. Harrison, Professor K. Teegarden, Dr. P. H. Yuster, and R. C. Sneed for their extremely helpful conversations concerning this work.

†Work supported by the Defense Advanced Research Projects Agency, under Grant No. DAH C15 73 and by the NSF under Grant No. NSF GH33630.

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