DOE/NV/01183--211-TP

S-211-TP

LOW-TEMPERATURE PHOTOLUMINESCENCE OF DETECTOR-GRADE HgI_2^*

by

DOE/NV/01183--211-TP

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ABSTRACT

The low temperature photoluminescence of HgI_2 is reported. Three main luminescence bands are observed, with peaks at ~ 2.30 , 2.20 , and 2.00 eV at 77 K. At 4.2 K, the highest energy peak shows considerable structure. The temperature dependence of these lines indicates both free and bound exciton recombination, and very small exciton binding energies (~ 3 - 5 MeV) have been estimated. A comparison of the results of sublimation and doping experiments suggests that the lowest energy band may be related to impurities, whereas the middle-energy band is related to I content. The two strongest bound exciton lines comprising the high-energy band show systematic correlations with the middle-energy, I-related band. Further correlations between these spectral features and the performance of nuclear radiation detectors fabricated from these samples are also noted. The temperature coefficient of the band gap is estimated from the spectral shift of luminescence lines to be approximately -1.13×10^{-4} eV/K between 32 K and 45 K.

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I. INTRODUCTION

HgI_2 is a wide bandgap, low melting point compound with tetragonal structure which has generated considerable interest in recent years as a nuclear radiation detector because of its large atomic number⁽¹⁾. At energies below 100 keV, its energy resolution approaches that of commercial Si and Ge detectors, and it enjoys the unique advantage of room temperature operation. At higher energies, however, detector performance is less promising. The material is still in an early stage of technological development, and it has been difficult to determine the physical mechanisms involved in radiation detection because of its high resistivity ($> 10^{13} \Omega\text{-cm}$), low carrier mobility ($\mu_e \sim 100 \text{ cm}^2/\text{Vsec}$; $\mu_h \sim 5 \text{ cm}^2/\text{Vsec}$), and lack of control over dopants, native defects, and inadvertent impurities. The resolution of detectors for high energy ($> 100 \text{ keV}$) gamma-rays appears to be limited by these problems. In order to evaluate the relative importance of defects and deep centers on carrier transport, several workers have carried out thermally stimulated conductivity (TSC) measurements^(2,3). These experiments remain somewhat inconclusive, however.

On the other hand, a great deal of investigation of the optical properties of HgI_2 has been reported. B.V. Novikov and M.M. Pimonenko⁽⁴⁾ (which will be referred to as NP in the remainder of this

paper) studied optical absorption and photoluminescence at low temperature, and reported on excitonic effects. Kanzaki and Imai⁽⁵⁾ observed three major exciton-like lines, referred to as A, B, and C, in the high energy region of the absorption spectrum. Anedda et al.⁽⁶⁾ found fine structure in the A exciton, and F. Sakuma et al.⁽⁷⁾ studied the phonon replicas of this exciton. There are several other papers dealing with low temperature photoluminescence of HgI_2 . Bube⁽²⁾ reported a photoluminescence spectrum of HgI_2 at 77°K consisting of three primary bands, the most intense of which was the lowest energy component. S. Nikitine and R. Kleim⁽⁸⁾ also observed three photoluminescence bands, but in their work the high energy band was the strongest. In addition, they found that the luminescent intensity decreased under constant excitation. Later, the same group⁽⁹⁾ observed that the high energy band consisted of two sharp lines at 4.2K, and suggested a simple exciton model to explain their experimental results. Using x-rays rather than ultraviolet light as an excitation source, E. Pinsky et al.⁽¹⁰⁾ obtained results that were very similar to those of Nikitine; at 9K they could not find any fine structure in the high energy band. NP did observe fine structure of the high energy band at 4.2K, and they were able to make assignments of some of the sharp lines to bound excitons and their phonon replicas. It is clear, both from the similarities and differences between so much of the luminescence work already reported, that very little control over crystal quality and impurity contamination has thus far been achieved.

This paper constitutes the first systematic report of the effect of crystal growth variation (including doping and stoichiometry changes) on the major features of the luminescence spectra; a preliminary report of

usually repeated a maximum of four runs (designated 1x, 2x, 3x, 4x^{*}). Further processing of this material was often performed before single crystal growth, including closed-tube melting of the 4x sublimed material (referred to as 4xM), which was sometimes followed by a subsequent closed-tube sublimation (referred to as 4xMS). The resulting material was then used as the source for the vapor-phase growth of large single crystals used for the fabrication of radiation detectors; suitable dopants could be added to the starting powder, if desired.

Low temperature photoluminescence was excited with the 5145Å^o green line from an Argon ion laser (50~100 mW). The samples were immersed in either liquid N₂ or in liquid He, which could be pumped below the λ point. Luminescence spectra were recorded using a McPherson 1 m monochrometer and an S-20 photomultiplier. Crystals were cleaved perpendicular to the C-axis. Before every measurement a reproducible etching procedure was followed to remove surface oxidation. The etching solution used for this purpose was 5% (by weight) KI in deionized (DI) water. In most cases, it took 3-5 minutes to remove the oxidation layer at room temperature, although this was dependent on the actual condition of the surface. It was found that the sample must be rinsed thoroughly in DI water immediately after etching, and that the transition from the etch solution to a DI water rinse must be done quickly. This "standard etching" procedure was found necessary to obtain intense, reproducible luminescence, as will be discussed below. Special care

* Note that we have departed from the convention employed in earlier papers, where these sublimations are referred to as 30x, 60x, 90x, and 120x, respectively. The original designations resulted from an attempt to estimate the actual number of sublimations involved in passing the powder the full length of the tube.

must be taken in handling the samples because of their extreme softness. Any contact with metal should be avoided, because the crystal reacts rapidly with metal, especially aluminum.

III. LUMINESCENCE RESULTS

A. Sublimation Experiments

A typical 77K spectrum is shown in Fig. 1, obtained from the Baker starting powder. Three bands are observed, which are characteristic of the material, and have been observed in single crystals by a number of workers.^(2,3,8-10) The relative strengths of these bands vary considerably, however, as was described in the Introduction, for samples prepared by different techniques, and even from sample to sample prepared in the same laboratory. For example, in the spectrum reported by Bube⁽²⁾, band 1 is the weakest, whereas band 3 is the strongest.

When this starting powder is subjected to the sublimation steps described above, two significant changes in the luminescence are observed, as shown in Fig. 2. (1) Band 3 becomes considerably weaker after the first sublimation run (1x); in fact, we have never observed band 3 after a 1x sublimation. Since the dominant effect anticipated for sublimation is the elimination of inadvertent impurities, we tentatively assign this band to impurity-related effects. However, we have thus far been unable to reproduce band 3 by doping experiments, as will be discussed in more detail below. There is some evidence (e.g., standard analysis) that our crystals contain a considerable concentration of carbon. (2) Band 2 increases dramatically relative to band 1 with each sublimation run, as is evident in Fig. 2. In fact, if one plots the ratio of band 2/ band 1 as a function of sublimation steps (using an

arbitrary distance along the horizontal axis; cf. inset to Fig. 2), a rapidly increasing function is observed. A similar result is obtained at 4.2K, shown in Fig. 3, where other processing steps (e.g., 4xMS) are included. Note that for both of these figures the horizontal axis is designated as decreasing I concentration; justification for this hypothesis will be given below.

B. Single Crystals

1. Surface treatments

The photoluminescence intensity of HgI_2 is extremely sensitive to surface treatment. We have carried out a series of tests showing the effect of different surface treatments on the luminescent spectra; this is shown in Fig. 4. When the surface was freshly cleaved and immediately immersed into liquid nitrogen, the luminescence intensity was strong. However, when these samples were removed from the liquid nitrogen and warmed to room temperature, the surface of the sample was usually moist, even if nitrogen-gas drying was employed. Upon re-immersing the sample into liquid nitrogen, we found that the luminescence intensity was considerably weaker (cf. Fig. 4, thermal cycle), implying that surface oxidation results in a significant decrease of photoluminescence intensity. However, the most intense luminescence could be observed after etching (as described above, Section II). We found that this etching procedure was necessary for obtaining intense, reproducible luminescence. If we slightly deformed the surface of the sample (for example, by pressing the sample with a Q-tip) the luminescence intensity decreased dramatically. For this reason considerable care was exercised to avoid deforming the sample, and the KI "Standard etch" was employed

immediately before all luminescence measurements. Note that band 1 is much more strongly affected by deformation, as expected, since band 1 emission is from near-gap (weakly bound) states.

2. Results at $T = 77K$

The results are somewhat different for single crystals grown from this sublimed material, as shown in Fig. 5. Band 1 is generally strong for single crystals, although its intensity is a function of doping. A series of samples was prepared for which the stoichiometry was influenced by adding excess I or Hg to the starting material. The growth conditions and the estimated relative doping expected for these samples are given in Table I.

Note that the sequence of samples A to F should constitute a decreasing concentration of I, or increasing Hg. Photoluminescence results for several of these samples are given in Fig. 5. The results clearly indicate that the band 2/band 1 ratio increases with conditions that are expected to lead to a relative loss of I, with one exception: sample A (heavily I). However, for sample A the overall luminescence intensity is anomalously weak, as shown by the dotted curve in the inset, so we believe that this sample is overdoped, resulting in low radiative efficiency. Of course, photoluminescence cannot provide quantitative information about the Hg or I content; nevertheless, we believe that the overall trend of the data is important: band 2 grows with decreasing I.

3. Results at $T \leq 4.2\text{K}$

At 4.2K and below, considerable structure has been observed for band 1, as shown in Fig. 6. Lines 1B and 1C are generally strong in most good single crystals. Lines 1A, 1B and 1C all show multiple longitudinal optical (LO) phonon replicas, while 1A* shows both longitudinal and transverse optical (TO) phonon replicas, as shown in Table II. For comparison, we have also listed the results of NP; the differences apparent in Table II, and comparison with other published results, will be discussed in detail in Section IV below. The energies of the LO and TO phonons are 14.0 meV and 2.3 meV, respectively, and have been determined with better precision than could be done by NP. Doublet 1A shows an anomalous temperature behavior, as will be described below. Because of the sharpness of these lines, their position near the bandgap, and the occurrence of various phonon replicas, we associate the structure of band 1 to various bound excitons. However, stress or magneto-optical experiments would be required to prove the specific exciton mechanism. The same bound exciton lines can also be seen in samples doped with Pb, Sb and Te, as will be discussed below, with no dramatic increase in intensity. We therefore assume that these exciton lines are at least unrelated to these specific impurities.

It is significant that the ratio 1B/1C of the two principal exciton lines differs considerably from sample to sample. Two quite different results are shown by the solid line (for which $1C \gg 1B$) and broken line ($1C < 1B$) in Fig. 7. There is a strong correlation between the strength of the line 1B and the intensity of band 2; this is also evident in Fig. 7. This correlation has been observed for a large number of samples. Fig. 8 presents a plot of the strength of 1B (relative to 1C)

as a function of band 2 intensity (which we have earlier correlated with probable loss of I), for most of the samples in the sequence A through F, and a large variety of samples for which no estimate of relative I content has been attempted. Exciton line 1B is clearly enhanced by the conditions which favor band 2. (Note again that sample A appears to be anomalous.) These data were obtained for good quality crystals; for poor quality crystals, 1B and 1C can not be resolved.

4. Temperature Dependence

In order to understand the fine structure, we have investigated the temperature dependence of individual lines. Fig. 9 shows the luminescence intensity of lines 1B and 1C as a function of reciprocal temperature for the case $1C \gg 1B$. The slope of the curve for line 1C gives an estimated binding energy of the exciton-defect complex of approximately 11.4 ± 0.4 meV, if we use the steepest portion of the curve (above 25K). Above 20K, line 1B cannot be resolved, and the intensity of 1C decreases rapidly. However, for the case $1B > 1C$, shown in Fig. 10, the slope of 1B is estimated to correspond to a binding energy of 2.6 ± 0.3 meV. Again above 20K, 1C merges into 1B, but 1B decreases slowly. Note that the data for line 1B in Fig. 9 and 10 are self-consistent.

The behavior of lines 1A and 1A* with temperature is quite different (Fig. 11). When the temperature rises from 4.2K, lines 1B, 1C and 1D, along with their phonon replicas, all become weaker; above ~45K, they all disappear. However, lines 1A* and 1A increase with temperature up to ~25K, reaching a maximum near this temperature, and then slowly decrease in intensity. These lines are still observable up to ~100K.

These characteristics strongly suggest free electrons: as the bound excitons are thermally liberated, the concentration of free excitons increases until thermal energy is sufficient to dissociate the free exciton. These results suggests that 1A is the free-exciton ground state, and $1A^*$ corresponds to a free-exciton excited state. (The reason for the doublet form of 1A is not understood; this may result from crystal effects, or simply be the ground and first excited state.) If we assume that the lower of the 1A doublet is the true free-exciton ground state (2.3332eV from Table II), then the binding energies of bound-exciton lines 1B and 1C are 3.2 and 4.6 meV, respectively, as listed in Table III. This should correspond to the values measured thermally: 2.6 and 11.4 meV, respectively. Agreement for line 1B is quite good. For line 1C, it appears that we should use the temperature region between 12 and 25K (the region where 1A increases with temperature) to estimate the binding energy of bound-exciton 1C. It is difficult to draw a straight line through the data in this region; however, our estimates give values of E_{Bx} as low as 2.5 meV, indicating that the true binding energy is substantially lower than 11.4 meV. On the other hand, the estimate of the free-exciton dissociation energy (1.2 meV) derived from the data of Fig. 11 is an underestimate of the true dissociation energy, probably because of the weak luminescent intensity of 1A above 50K.

If we assume that the binding energy of an exciton-defect complex varies much more slowly with temperature than that of bandgap,⁽¹²⁾ (as is usually the case with semiconductors), the spectral shift of line 1C is mainly due to the change of bandgap. Therefore, the temperature coefficient of the bandgap can be estimated from Fig. 12. The result is

-1.13×10^{-4} eV/K in the temperature range 30~45K. This value is smaller than the average value -2.6×10^{-4} eV/K obtained by other workers over a wider temperature range (see Table IV). Below 30K the bandgap remains unchanged, as is found for most semiconductors.

5. Crystals from other Laboratories

Besides the EG&G crystals grown by TOM in the laboratory of two of the authors (LvdB and WFS), we have made preliminary luminescence measurements on a small number of crystals provided by other laboratories. One sample, LETI18-1, was obtained from I.F. Nicolau, C.E.S.-C.E.N.G., Grenoble, France. The physical appearance of this sample was excellent, but at 4.2K, lines 1B and 1C were unresolvable. The intensity of band 2 was moderate.

Fig. 13 shows the spectra of samples designated U-30 and U-33, provided by F. Rosenberger at the University of Utah, along with EG&G sample S3-10 for comparison. At 77K, the luminescence intensity of the Utah samples is weak relative to S3-10. Band 1 of U-33 is shifted approximately 6 meV to lower energy with respect to sample U-30, and band 3 is observable. (Note that band 3 is not observed in EG&G crystals, only in the starting powder.) However, both Utah samples are very uniform: very little change is observed in the luminescence spectrum as the position of the laser excitation is moved on the sample. This is generally not the case for EG&G samples. The Utah samples were also characterized by Rosenberger as extremely uniform, using light scattering techniques. At 4.2K, the spectra of samples U-33 and U-30 are slightly different. Lines 1B and 1C are observed in both samples, although at different relative intensities and at slightly different

energies, as shown in Fig. 14. Additional fine structure can be identified (1A-L0, 1C-L0), although this structure is broadened and difficult to compare with EG&G samples. Furthermore, there was some evidence of instability for the Utah samples: after one month in a dessicator, the surfaces of the samples turn a grey color; this has not been observed for EG&G samples.

6. Preliminary doping experiments

As mentioned above, we have been unable to reproduce band 3 by any doping experiments. Before growing crystals, various dopants, such as SbI_3 , PbI_2 or TeI_4 , were added to the sublimed material (usually 4xMS) as the source for growing crystals. The growth of single crystals then takes place at a temperature that is so low (about 112°C) that it is uncertain whether or not these and other impurities are actually incorporated into the HgI_2 crystal. We could not see band 3 in any of these doped samples. The spectra were nearly identical to undoped samples, with the exception that the luminescence intensity was usually weaker in the doped samples.

Attempts were also made to dope the starting powder by adding impurities (e.g.: NaI or SbI_3) to the 4x sublimed powder before melting and further closed-tube sublimation (4xMS). In this case, the photoluminescence spectra were strongly dependent on excitation intensity. At 77K, the intensity of band 1 was found to increase with exciting power faster than band 2. At low exciting power (30 mW), band 2 was stronger than band 1; at high exciting power (300 mW), band 1 was stronger. In undoped 4x sublimed powder, band 2 is always much stronger than band 1, as shown in Fig. 2.

7. Polarization effects

Because of its tetragonal crystal symmetry, the optical absorption spectrum of HgI_2 depends on the orientation of the electric field vector of the incident radiation with respect to the C-axis.⁽¹³⁾ In the $E \perp C$ configuration at 4.2K, only the continuous absorption edge can be seen, whereas for $E \parallel C$ the absorption spectrum shows fine structure. In this work we have briefly investigated the polarization properties of the photoluminescence. Photoluminescence was measured for $E \perp C$, and for a component of $E \parallel C$, at 4.2K. No appreciable difference was observed. Furthermore, the emitted luminescence was found to be unpolarized. Thus, no additional useful information was forthcoming from these polarization measurements.

IV. DISCUSSION

A. Excitonic Behavior

The results at low temperature ($1.6\text{K} \leq T \leq 4.2\text{K}$) indicate that band 1 consists of a number of sharp lines, which we have associated with excitonic effects. The two strongest of these lines are most likely bound excitons, and the strongly-suggestive relations observed between the strength of these lines relative to other spectral features and doping with Hg or I will be discussed below. The rich spectral region between 2.30 eV and 2.34 eV has been studied in detail, and assignments for several of these lines have been made based on their energy and their behavior with temperature. Phonon replicas up to 3LO-T0 have been identified. Many of these same lines were observed in undoped HgI_2 earlier by NP although with considerably lower spectral resolution. These data are compared in Table II.

Comparison of the results of NP and those reported here reveals two major differences. (1) From the temperature dependence of the luminescence intensity, we argue that the doublet line 1A is most likely the free exciton, and have assigned a weak, higher energy line ($1A^*$) as an excited state of the free exciton. In our study, 1A and $1A^*$ behave in very similar fashion, both have a strong phonon coupling, and both display an anomalous temperature behavior compared with the other (stronger) bound exciton lines. Using 1A as the free exciton, we then estimated binding energies for the dominant bound excitons, and found reasonable agreement with their temperature behavior. NP, on the other hand, argue that the line they call λ_1 (which appears to correspond to 1A) is a bound exciton, despite the fact that they see the same anomalous temperature behavior. They base their argument on the observation

of three strong lines in the absorption spectrum which appear to fit a Rydberg series for the $n = 1, 2$, and 3 states of the exciton, with the $n = 1$ ground state corresponding to our $1A^*$ line. By fitting this Rydberg series, they estimate that the free exciton binding energy is 29 meV, and go on to estimate the effective mass and radius of the exciton ground state to be $0.13 m_0$ and $25\text{\AA}$, respectively. Both arguments have merit, but we find it hard to explain the anomalous temperature dependence of $1A$ in terms of a bound exciton. The spectral resolution obtained by NP is considerably less than that used here.

(2) A second major difference between NP and the work reported here concerns the two dominant bound excitons. Even a casual inspection of the data strongly suggests the correlation of line $1B$ with that designated λ_x by NP, and $1C$ with λ_2 . However, in our work it is the higher energy line $1B$ that correlates with band 2 and decreasing I , whereas for NP it is the lower energy line λ_2 that shows this same correlation. Note that NP describe this line as correlated with the edge luminescence at $5600\text{\AA}$, and assume that it is due to "intrinsic" nonstoichiometry because it has been observed by many workers for many crystals grown in different ways.

We have, at this point, no obvious explanation for the differences noted above, other than to point out that the entire spectrum reported by NP appears to be superimposed on a broad band, and that the various spectral features are not well resolved. It is therefore difficult to distinguish between the two dominant excitons, λ_x and λ_2 , in terms of intensity correlations. It is also possible that there are small errors in determining the absolute energies of these spectral lines, and that λ_x represents an exciton bound to an impurity not present in the EG&G crystals, so that $1B$ and λ_2 are indeed identical.

Kleim et al.⁽⁹⁾ have also reported excitonic effects in HgI_2 . They observe two lines, designated A and B. Line A corresponds to the doublet 1A in our work, and is observed by Kleim et al. to have the same anomalous temperature dependence, and is therefore assigned by them as a free exciton. Line B is broader than those observed in this work, but corresponds to an average of 1B and 1C; this line decreased with increasing temperature, and is designated as a bound exciton with estimated binding energy of ~ 4 meV, in good agreement with our results (cf. Table III).

There is a possibility that the first LO phonon replica of the doublet 1A is actually a different no-phonon bound exciton line, since the phonon replicas do not appear to be at quite the right energy. In fact, the LO phonon replicas of 1A were omitted in calculating the RMS deviation for the LO phonon energy (cf. Table II) since the resulting phonon energy was 14.0 ± 0.2 meV without them, and 14.0 ± 1.0 meV if they are included. The coincidence of these doublets at nearly the same LO energy suggests, however, that these are indeed phonon replicas rather than a new bound exciton line, and that the energy deviations noted simply reflect the difficulty of accurately measuring the energies of weak doublets. We also suspect that the lines designated λ_0 -LO-TO and λ_0 -2LO-TO by NP (Table II) are really the higher energies of λ_1 -LO and λ_1 -2LO (i.e., replicas of our doublet 1A).

B. Stoichiometry

Based on the changes of luminescence intensity of bands 1 and 2 with changes in the Hg/I ratio of doped single crystals, it is tempting to infer information about stoichiometry from the sublimation experiments (Fig. 2 and 3). Although the sublimation process eliminates

impurities, we suspect that sublimation also reduces the iodine concentration of the material by the preferential removal of the more volatile species, I. The growth of band 2 in powder samples subjected to successive sublimation steps (Fig. 2 and 3), and in single-crystal samples for which the I concentration is seriously affected by Hg and I doping (Fig. 5), is consistent with this hypothesis. It is for this reason that the horizontal axis of Fig. 2 (inset) and Fig. 3 are designated "decreasing I". Note that the additional samples plotted in Fig. 3 (4xM and 4xMS) were processed in a sealed tube, under conditions for which the above simple arguments about preferential I removal are invalid. Therefore, although these treatments were performed on 4x material, it is consistent with all other results to plot their data on the left of the diagram, corresponding to relatively large I composition.

The above experiments suggest a correlation between relative changes in I (or Hg) composition and major features in the luminescence spectra; however, no statement can be made about the actual stoichiometry of these materials. The stoichiometry of single crystal HgI_2 is currently a topic of considerable controversy. Nicolau and Roland⁽¹⁴⁾ have analyzed a variety of crystals grown by TOM, vapor phase, and grown from solution. By using both the lattice constant-density method, and measurements of phase-transition temperature, they report stoichiometry deviations on both the Hg- and I-rich sides. Dishon et al.⁽¹⁵⁾ found only the iodine-rich case by Rutherford backscattering measurements on crystals obtained from Nicolau. Different analytical techniques thus appear to yield different results for the same samples. Using a chemical method which is a modification of the procedure given by ACS Reagent Chemical Specifications, DeLong and Rosenberger⁽¹⁶⁾ analyzed a number of

EG&G samples, as well as the samples from their own laboratory (referred to as "Utah" samples in Section III.B.5). In no case did they measure an excess of I. They report results on some of the same samples used in this work (samples D, E, and F in Table I and Figs. 5 and 8), and find decreasing I for the samples in that order, in agreement with our results. On the other hand, they also find that repeated sublimation decreases the Hg concentration, rather than the I concentration, as suggested by our experiments. This result is supported by work of Nicolau.⁽¹⁷⁾ DeLong and Rosenberger claim that all of the samples they have investigated are I-deficient, whereas our results suggest only relative changes in I concentration. In general, much of the available evidence discussed above suggests a correlation between dominant features in the luminescence spectra (line 1B, band 2) and Iodine loss in the samples. Furthermore, it has been pointed out that commercial reagent-grade HgI_2 powder must usually be purified and iodine-treated⁽¹⁸⁾ to obtain good radiation detectors.

C. Luminescence correlation with detector performance

One of the primary motivations of this luminescence investigation of HgI_2 is the hope of correlating the fundamental material properties with the device performance of radiation detectors fabricated from this material. We have carried out such studies, and, in general, we have found that good detectors are usually made of single-crystal material that is lightly doped with iodine, and which has a strong near bandgap emission (band 1), and a relatively weak band 2, such as sample B in Fig. 5. From the low temperature photoluminescence spectra we can correlate the performance of good detectors with a weak 1B/1C ratio, and

a weak band 2 (i.e., lower left portion of Fig. 8). However, this appears to be only a trend, and a number of exceptions have also been observed. For example, good-quality detectors have been fabricated from crystals S8-7 and S8-10, which fall right in the middle of Fig. 8. Recently, we have measured photoluminescence from large, detector-sized (1 cm^2), sawn and polished wafers from sample S8-14. The luminescence was found to be strong and uniform in the central region of the wafer, though weaker and broader near the edges, which might be due to processing damage. The spectrum was dominated by line 1C. According to the point of view presented above, one might expect to be able to make good detectors from this crystal. That has proved to be the case.

We also performed low temperature photoluminescence measurements on actual devices (with electrical contacts), which have been evaluated as radiation detectors. A sufficiently large border around the contacts was left exposed so that luminescence measurements could be made in this region, and a transparent passivating cap was employed. The most significant result of the experiment, however, was that luminescence from actual detectors has thus far been found to be extremely non-uniform; large variations in intensity were noted as the exciting beam was moved about the non-contacted region of the detectors. Furthermore, in some regions band 1 was too broad to resolve the structure of lines 1B and 1C. Nevertheless, of three devices investigated, the best detector had the lowest 1B/1C ratio (less than unity), consistent with the trend noted above.

V. CONCLUSIONS

The sharp, exciton-like lines with phonon replicas just below the bandgap have been studied in detail, and differences noted with earlier published work. Through measurements of their temperature dependence, these lines have been identified as resulting from the radiative recombination of bound or free excitons, and very small exciton binding energies ($\sim 3\text{-}4$ meV) have been estimated. The chemical and/or defect nature of these exciton binding sites is at present unknown; systematic doping experiments still have to be carried out.

Two of the exciton lines, 1B and 1C, dominate the low-temperature photoluminescence. A strong correlation has been noted between the shallower of these lines (1B) and a lower energy luminescence band (band 2). A third, deep band (band 3), reported by earlier investigators, is observed only in the pre-processed HgI_2 starting powder used for crystal growth. The intensities of line 1B and band 2 increase under conditions which, at least from simple arguments, would seem to favor a decrease in I concentration in the material. Present information concerning the stoichiometry of HgI_2 is controversial, but a consistent trend concerning the need for additional I in good-quality material has been noted.

The photoluminescence data presented in this paper suggest a model that correlates the quality of HgI_2 radiation detectors with increasing I content, suggesting that either I vacancies or Hg interstitials might lead to trapping centers which reduce the collection efficiency of these devices. However, this model is highly speculative, since the actual stoichiometry could be a much more complicated function of the crystal preparation than has been assumed in these simple considerations. From

luminescence measurements on actual devices, it is suggested that (a) special care should be exercised in processing HgI_2 in order to avoid mechanical damage due to the extreme softness of the crystals, and (b) the addition of I may improve detector performance. However, from luminescence results alone, nothing can be inferred about absolute crystal stoichiometry.

One last point seems appropriate. The dominance of native defects in determining the electrical and optical properties of other wide bandgap materials, the II-VI compounds, has long been assumed; only recently have experiments been performed which suggest that inadvertent impurities may, in fact, be of comparable importance for the device characteristics of these materials. The studies described above also emphasized stoichiometry or native-defect effects, but attempts to change stoichiometry may also cause large changes in impurity contamination. Controlled, systematic doping experiments, along with additional studies of trapping centers, are of paramount importance if further progress is to be made in our understanding of this material.

ACKNOWLEDGEMENTS

The authors would like to thank M. Mizuta and N.H. Sheng for assistance and technical discussions concerning all phases of these experiments, C. Ortale, L. Padgett, and D. Zak for experimental assistance, and I.F. Nicolau and F. Rosenberger for supplying us with samples as well as discussing our results.

REFERENCES

1. R.C. Whited and M.M. Schieber, Nucl. Instr. and Methods 162, 113 (1979).
2. R.H. Bube, Phys. Rev. 106, 703 (1957).
3. R.C. Whited and L. van den Berg, IEEE Transactions on Nuclear Science, NS-24, 165 (1977).
4. B.V. Novikov and M.M. Pimonenko, Soviet Physics-Semiconductors 4, 1785 (1971).
5. K. Kanzaki and I. Imai, J. Phys. Soc. Japan 32, 1003 (1972).
6. A. Anedda, F. Raga, E. Grilli and M. Guzzi, Nuovo Cimento 38B, 439 (1977).
7. F. Sakuma, M. Fukutani and G. Kuwabara, J. Phys. Soc. Japan 45, 1349 (1978).
8. S. Nikitine and R. Kleim, Physics Lett. 20, 341 (1966).
9. R. Kleim, F. Raga and S. Nikitine, Proc. of International Conference on Luminescence, p. 1496 (1966).
10. E. Pinsky, A. Halperin, I. Beinglass and M. Schieber, IEEE Trans. Nucl. Sci. NS-24, 260 (1977).
11. Z.L. Wu, J.L. Merz, L. van den Berg and W.F. Schnepple, Proc. Intl. Conf. on Luminescence, ed. by I. Broser (North Holland Publ. Co., 1981); J. Luminescence 24/25, 197 (1981).
12. B.V. Novikov and M.M. Pimonenko, Soviet Physics-Semiconductors 6, 671 (1972).
13. S. Nikitine, Progr. Semicond. 6, 269 (1962).
14. I.F. Nicolau and G. Rolland, to be published.
15. G. Dishon, M. Schieber, L. Ben-Dor and L. Halitz, Mat. Res. Bull. 16, 565 (1981).

16. M.C. DeLong and F. Rosenberger, HgI_2 Workshop, Santa Barbara, CA, 1981.
17. I.F. Nicolau, private communication.
18. I. Beinglass, G. Dishon, A. Holzer and M. Shieber, J. Crystal Growth 42, 166 (1977).

Table I. Growth conditions and estimated doping resulting from the addition of I_2 or Hg to the starting material.

Growth Conditions		Doping	Crystal No.
A	100 g HgI_2 + I_2 (22°C)	Heavily-doped I_2	(S3-7)
B	100 g HgI_2 + I_2 (0°C)	Lightly-doped I_2	(S3-10)
C	100 g HgI_2	Typical undoped	(S1-6)
D	100 g HgI_2 + 0.4 μ l Hg	Lightly-doped Hg	(S3-4)
E	100 g HgI_2 + 2.0 μ l Hg	Moderately-doped Hg	(S1-4)
F	100 g HgI_2 + 5.0 μ l Hg	Heavily-doped Hg	(S2-23)

Table II. Fine structure of band 1 at low temperature. Comparison is made with the results of Novikov and Pimonenko (ref. 4). See text for discussion of apparent differences between this work and ref. 4.

This Work (1.6K)

Ref. 4 (4.2K)

Line	Energy (eV)	Assignment and Comments	Line	Energy (eV)	Assignment and Comments
1A*	2.3402	Free exciton excited state	λ_0	2.340	Free exciton; strong absorption
1A	2.3379 2.3332	Doublet; Free exciton ground state; Increases with T	λ_1	2.335	Bound exciton; Increases with T
1B	2.3300	Dominant bound exciton; Increases with band 2 (5600A); Decreases with increasing T.	λ_x	2.331	Dominant bound exciton; Decreases with increasing T
1C	2.3286	Dominant bound exciton; Decreases as band 2 increases; Decreases with increasing T	λ_2	2.329	Dominant bound exciton; Increases with 5600A band; Decreases with increasing T; Due to "intrinsic" stoichiometry
1A*-LO	2.3262		λ_0 -LO	2.326	
-	-		λ_0 -LO-TO	2.323	
1A-LO	2.3214 2.3198		λ_1 -LO	2.319	
1B-LO	2.3162		λ_x -LO	2.317	
1C-LO	2.3144		λ_2 -LO	2.315	
1A*-2LO	2.3120		λ_0 -2LO	2.313	
-	-		λ_0 -2LO-TO	2.310	
1A-2LO	2.3105 2.3083		λ_1 -2LO	2.308	
1B-2LO	2.3022		-	-	
1C-2LO	2.3012		λ_2 -2LO	2.303	
1A*-3LO	2.2977		λ_0 -3LO	2.298	
1A*-3LO-TO	2.2959		λ_0 -3LO-TO	2.296	

Table III. Exciton Binding Energies, and phonon energies. E_x is the dissociation energy of the free exciton, as derived from the lower-energy component of doublet 1A. E_{Bx} is the binding energy of each bound exciton. The phonon energies were derived using assignments and energies given in Table II.

	<u>Spectral Line</u>	<u>Energy below 1A (meV)</u>	<u>Thermal Activation (meV)</u>	<u>Ref. 4 Energy below λ_o (meV)</u>
E_x	1A	-	(1.2)	
E_{Bx}	1B	3.2	2.6	5
E_{Bx}	1C	4.6	2.5-11.4	11
Phonon energies derived from Table II:				
		<u>This work</u>	<u>Ref. 4</u>	
LO		14.0 ± 0.2^1	14.0 ± 0.9	
TO		2.3^2	2.3 ± 0.6	

¹ LO replicas of 1A were ignored in calculating RMS deviation.

² Single data point; RMS deviation undefined.

Table IV. Temperature coefficient of bangap.

Coefficient	Temperature Range	Ref.
-1.13×10^{-4} eV/K	30~45 K	this work
-2.6×10^{-4} eV/K	20-77 K	12
-7.0×10^{-4} eV/K	100-200 K	2
-14×10^{-4} eV/K	300-400 K	2

FIGURE CAPTIONS

- Fig. 1 Photoluminescence spectrum of HgI_2 powder (Baker reagent-grade) at 77K before sublimation. The three bands identified are often observed in HgI_2 , but with widely different intensities.
- Fig. 2 Photoluminescence spectra of HgI_2 powder at 77K, after various sublimation steps. The designations Nx ($N = 0, \dots, 4$) refer to the number of times the powder is passed along the sublimation tube (cf. text). The broken line (0x) is the same spectrum as that shown in Fig. 1. The inset shows the intensity ratio of band 2/band 1 for successive sublimation runs, using an arbitrary scale along the horizontal axis. The legend "decreasing I" will be explained in the text.
- Fig. 3 Intensity of band 2 at 4.2K vs. sublimation runs. 4xM is 4x material melted in a sealed tube. 4xMS is 4xM followed by a subsequent closed-tube sublimation.
- Fig. 4. Effect of various surface treatments (which are described in the text) on the luminescence intensity of bands 1 and 2.
- Fig. 5 Photoluminescence of doped HgI_2 single crystals at 77K. Inset shows band 2/band 1 ratio, and intensity of band 1, for samples doped with Hg and I_2 (cf. Table I).
- Fig. 6 High resolution luminescence spectrum showing the fine structure of band 1 at 1.6K. Various LO phonon replicas are indicated. Inset shows the relative intensity of 1B and 1C.
- Fig. 7 Detail of band 1 (with fine structure) and band 2 luminescence showing two distinct cases which are frequently observed: (a) $1C < 1B$ with strong band 2 (broken line), and (b) $1C > 1B$ with weak band 2 (solid line).

- Fig. 8 Ratio of luminescence lines 1B/1C vs. intensity of band 2, which has been correlated with decreasing I (cf. text). A small 1B/1C ratio corresponds to weak band 2 luminescence. Good nuclear radiation detectors are often fabricated from material in the lower left corner of this diagram.
- Fig. 9 Luminescence intensity of lines 1B and 1C, as a function of reciprocal temperature. The slope of the curve at high temperature should give an estimate of exciton binding energy. These data were obtained from a crystal for which $1C > 1B$.
- Fig. 10 Luminescence intensity of lines 1B and 1C as a function of reciprocal temperature for a case where $1B \geq 1C$, allowing estimation of 1B binding energy.
- Fig. 11 Luminescence intensity of doublet line 1A as a function of reciprocal temperature. The increase of 1A with increasing T between 10 and 25K suggests free-exciton behavior.
- Fig. 12 Dependence of the energy gap of HgI_2 as a function of temperature, between 4 and 44K.
- Fig. 13 Photoluminescence spectra of crystals U-30 and U-33 obtained from the University of Utah, at 77K. The luminescence intensity is relatively weak compared with most of the EG&G samples studied in this work.
- Fig. 14 Photoluminescence spectra of U-30 and U-33 at 4.2K.

Figure 1

Figure 2

Figure 3

Figure 4

S-211-TP

Figure 6

Figure 7

Figure 8

S-211-TP

Figure 9

Figure 10

REL. LUMINESCENCE INTENSITY

Figure 11

Figure 12

S-211-1P

Figure 13

Figure 14