

DEEP-LEVEL PHOTOLUMINESCENCE OF $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$

A Thesis

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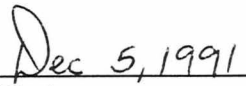
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This thesis by Cheryl Barnett Davis is accepted in its present form by the Department of Physics of Brigham Young University as satisfying the thesis requirement for the degree of Master of Science.


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I. INTRODUCTION AND BACKGROUND

Zinc cadmium telluride ($\text{Zn}_x\text{Cd}_{1-x}\text{Te}$) is a direct band gap semiconductor with possible applications in near-infrared optical electronic devices such as lasers, photovoltaic and photoconductive infrared detectors, high-efficiency solar-cell structures, and electroluminescent devices. $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ is also a new substrate material for the epitaxial growth of mercury cadmium telluride ($\text{Hg}_{1-y}\text{Cd}_y\text{Te}$). High crystalline quality is needed for use as a substrate. Defects in the substrate often cause defects in the epitaxial layers. $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ is a good substrate material because its lattice parameters can be matched to those of $\text{Hg}_{1-y}\text{Cd}_y\text{Te}$; thus, defects due to "misfit-dislocation" are minimized.¹ $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ is also useful for formation of superlattices in combination with other II-VI compounds. For these applications the annealing behavior and the identification and elimination of impurities is essential.² This material has a narrow band gap that is tailorable from that of cadmium telluride, CdTe (1.44 eV at room temperature), to that of zinc telluride, ZnTe (2.26 eV at room temperature). It has the same characteristics as other direct band gap semiconductors with the added advantage that its band gap ranges from the infrared into the visible. Its study as an electronic material is in its infancy.

A great deal of effort has been expended in studying $\text{Hg}_{1-y}\text{Cd}_y\text{Te}$ and other similar materials, but $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ has not been investigated to any great extent. This deficit is mainly due to the lack of experimental work in the infrared region and the lack of high-quality samples. Basic research on the typical photoluminescence spectrum of CdTe has been done. The spectrum for $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ is similar except that the emission lines are all shifted to higher energies (shorter wavelengths) and the bound exciton lines are broader than in CdTe.¹ I have duplicated the typical photoluminescent spectrum results cited in the literature for CdTe and $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ in order to investigate sample quality and verify that the equipment was functioning properly.

In my investigation I have also noted a peak in the mid-gap region (1.1 eV) for certain samples that has not been studied. This peak is probably due to impurities or defects in the sample. It may be useful in the identification of different impurities. I have tried to determine the source of this peak and to better characterize the $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ spectrum.

This study is limited to the photoluminescent spectrum. It does not yield general conclusions on $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$. I examined the cause of the far-infrared peak and of other changes in the spectra, whether these are due to surface or bulk defects, and how these features depend on zinc concentration, surface preparation, and annealing.

II. FUNDAMENTAL THEORIES

A. Absorption

The absorption process takes place when a photon of a known energy excites an electron from a lower energy state to a higher excited energy state. The light consists of photons of energy $h\nu$ and momentum $\hbar k$. An electron in the valence band of the semiconductor absorbs the photon and gains an additional energy $h\Delta\nu$ and momentum $\hbar\Delta k$. This allows the electron to move in k -space by an amount Δk . If the energy of the light is less than the band gap energy of the semiconductor, the electron will not absorb the photon because the electron cannot occupy a state in the gap. Therefore, the minimum energy of absorption--the absorption edge--is E_g , the band gap energy. At the energy gap there is a rapid rise in absorption. If the energy is too large, the electron will escape the crystal. These limits give a range of possible photon energies, which correspond to a range of wavelengths of light, that will be absorbed by a certain semiconductor.³ Absorption is measured by looking at the radiation transmitted through a semiconductor at different energies. The absorption intensity, $L(h\nu)$, is expressed in terms of the absorption coefficient α

$$\alpha = \frac{1}{L(h\nu)} \frac{d[L(h\nu)]}{dx}. \quad (1)$$

The absorption coefficient for a given transition is proportional to the probability, P_{if} , of a transition multiplied by the density of electrons in the initial and final states, n_i and n_f , respectively. To calculate the total absorption coefficient take the sum of this product over all possible initial and final states. Thus, the equation becomes

$$\alpha(h\nu) = A \sum P_{if} n_i n_f \quad (2)$$

where A is a proportionality constant that is a function of the electron and hole reduced masses.

An allowed direct transition is a transition between two direct valleys where momentum is conserved. For this case P_{if} is independent of the photon energy. The energy is given by the conservation of energy equation

$$E_f - E_i = h\nu. \quad (3)$$

The energies are the initial and final energies of the state in the semiconductor, and the energy difference is that of the absorbed photon. The valence and conduction band edges are approximated as parabolas in energy versus the k vector in reciprocal space. CdTe is a direct gap semiconductor; that is, the maximum energy of the valence band is directly below the minimum energy of the conduction band in k -space (reciprocal space). The parabolic approximation for the bands yields

$$E_f - E_g = \frac{\hbar^2 k^2}{2m_e^*} \quad \text{and} \quad (4)$$

$$E_i = -\frac{\hbar^2 k^2}{2m_h^*} \quad (5)$$

where the masses m_e and m_h are the effective masses of an electron and of a hole, respectively. Now equation (3) can be written

$$E_g + \frac{\hbar^2 k^2}{2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) = h\nu. \quad (6)$$

P_{if} , and thus α , is proportional to the density of states. The density of directly associated states is

$$N(h\nu)d(h\nu) = \frac{8\pi k^2 dk}{(2\pi)^3} \quad (7)$$

$$= \frac{(2m_r)^{3/2}}{2\pi^2 \hbar^3} (h\nu - E_g)^{1/2} d(h\nu) \quad (8)$$

where m_r is the reduced mass given by

$$\frac{1}{m_r} = \frac{1}{m_e^*} + \frac{1}{m_h^*}. \quad (9)$$

The absorption coefficient is

$$\alpha(h\nu) = B(h\nu - E_g)^{1/2} \quad (10)$$

where

$$B \approx \frac{q^2 \left(\frac{2m_h^* m_e^*}{m_h^* + m_e^*} \right)^{3/2}}{nch^2 m_e^*}, \quad (11)$$

q is the charge of an electron, n is the index of refraction, and c is the speed of light.^{4, 5}

B. Emission

The emission of light is the reverse process. It takes place when an electron in an excited state falls into a lower energy state and emits a photon with the extra energy. This requires some excitation method to initially excite the electrons. In photoluminescence processes, light--usually from a laser--is used to excite the electrons in the sample. The rate of emitted radiation is proportional to the probability P_{ul} for one carrier/cm³ in the upper state to make a radiative transition to one vacancy/cm³ in the lower state. This value is multiplied by the density of carriers in the upper and lower states, given by n_u and n_l , respectively. In equation form,

$$R = n_u n_l P_{ul}. \quad (12)$$

This equation gives the rate of photon generation per unit volume. The radiative recombination rate is related to the absorption coefficient (at thermal equilibrium) according to the equation

$$R(\nu)d\nu = \frac{\alpha(\nu)8\pi\nu^2n^2}{c^2[e^{h\nu/kT}-1]}. \quad (13)$$

Emission occurs over a much more narrow spectral range than absorption because the absorption process can involve all the states in a semiconductor, but the emission process is limited to the states involving thermalized electrons and thermalized holes.⁶ Possible transitions include band-to-band, free excitons, bound excitons, impurity, donor-acceptor pair transitions, and phonon replicas of these same transitions.

1. Band-to-Band Recombinations

Band-to-band recombinations are transitions between the valence band and the conducting band of the material. Thus, the energy of this transition is equal to or greater than the band gap energy. When free carriers that occupy band states recombine and radiate a photon, a band-to-band transition results. The allowed direct transitions give an emission spectrum analogous to that obtained for absorption for the same transitions:

$$I(\nu) = D(h\nu - E_g)^{1/2} \quad (14)$$

where I is the emission intensity and

$$D = \frac{2q^2(m_r^*)^{3/2}}{nch^2m_e^*}. \quad (15)$$

This equation gives a low-energy threshold of E_g . The energy of the photons emitted in these transitions increases with an increase in temperature or excitation rate because states higher in the conduction band become filled. Electrons in higher excited states fall to states in the valence band and give off higher energy photons.⁷ I do not see photons due to direct band-to-band recombination.

2. Exciton Recombination

There are two types of excitons: free excitons and bound excitons. A free exciton consists of a free hole and a free electron that are bound with respect to one another by the mutual coulomb attraction. Because of this attraction the electron orbits the hole similar to a hydrogen-like atom or, even more closely, since mutual annihilation is possible, like a positronium atom. Free excitons can wander through the crystal. Impurities in a sample can cause the excitons to dissociate. The ionization energy of the free exciton is

$$E_x = -\frac{m_r^* q^4}{2h^2 \kappa^2 n^2} \quad (16)$$

where n is an integer = 1, 2, 3,... for various exciton states, κ is the macroscopic dielectric constant of the material, and m_r^* is the reduced mass in the equation

$$\frac{1}{m_r^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*}. \quad (17)$$

The exciton ionization energy is lower than the donor-acceptor transitions (to be discussed next) because m_e^* and m_h^* are in the same order of magnitude.⁸ Equation three then yields

$$E_g - E_x = h\nu. \quad (18)$$

This energy is about 10.5 meV less than the band gap energy.¹

A free exciton trapped at impurities and structural defects becomes a bound exciton. There are many different types of bound excitons with different combinations of electrons, holes, donors, and acceptors.⁹ An example is an electron bound to a neutral donor so that it orbits the donor. Then a free hole that is attracted to the electron also orbits the donor. The binding energy of a bound exciton is higher than the free exciton binding energy due to the binding energy of the exciton to the impurity. Thus the emitted photon has a lower energy than that of the free exciton. The ionization energy for the bound exciton becomes

$$E_i = E_x + E_b \quad (19)$$

where E_b is the binding energy of the exciton to the impurity and E_x is the free exciton binding energy. The general equation for the energy of the emitted photon then becomes:

$$E_g - E_x - E_b = h\nu. \quad (20)$$

The line width of the bound exciton is also narrower than that of the free exciton. When the temperature of the sample is increased, the intensity of the bound exciton peaks decrease according to the equation

$$\frac{L(T)}{L(0)} = \frac{1}{1 + CT^{3/2} \exp(-\frac{E_i}{kT})} \quad (21)$$

where C is a constant. This equation can then be used to solve for E_i .¹⁰

3. Band-Impurity Transitions

Impurities act as either donors or acceptors in the semiconductor. The donor energy state is an energy, E_d , below the bottom of the conduction band, and the acceptor energy state is an energy E_a above the maximum of the valence band. The donor ionization energy E_d is

$$E_d = \frac{m_e q^4}{32\pi^2 \hbar^2 \kappa^2}. \quad (22)$$

The acceptor ionization energy E_a is given by the same equation except that m_e is replaced by m_h .^{11, 12} There are two types of transitions between a band and an impurity level, shallow transitions and deep transitions.¹³ A shallow transition is that of an electron from the conduction band to a donor state or from an acceptor state to the valence band. The emitted photon energies E_d are

$$E_d = h\nu_d \text{ and } E_a = h\nu_a \quad (23)$$

These energies are small; thus, the peaks due to these transitions are in the far-infrared region. The probability of these transitions emitting a photon is much smaller than that of emitting a phonon, which condition makes them difficult to detect.

A deep transition is that of an electron from the conduction band to an acceptor state or from a donor state to the valence band. These transitions are best seen if the impurity concentration in the semiconductor is low. In most direct gap semiconductors the electron effective mass is smaller than the hole effective mass. This difference makes the donor ionization energy, E_d , lower than the acceptor ionization energy, E_a . The equations for the energy of the photons are

$$E_g - E_d = h\nu_d \text{ and} \quad (24)$$

$$E_g - E_a = h\nu_a. \quad (25)$$

Thus, the donor-to-valence-band transition emits a photon of higher energy than does the conduction-band-to-acceptor transition. As the impurity concentration increases, the emission spectrum broadens and shifts slightly toward lower energy due to an apparent shrinkage of the energy gap. There can be various donor and acceptor levels giving rise to several peaks in the emission spectrum.¹⁴

4. Donor-Acceptor Pair Transitions

Donors and acceptors, which form pairs and act somewhat as stationary molecules imbedded in the crystal, are called donor-acceptor pairs. The coulomb interaction lowers their binding energies according to the equation

$$E_{pair} = E_g - E_d - E_a + \frac{q^2}{\kappa r} \quad (26)$$

where r is the separation.¹⁵ There are many different states possible because the distance between the donors and acceptors varies from neighboring pairs to very distant pairs. In non-elemental semiconductors, there are two types of D-A pairs, type-I and type-II, depending on the sublattice occupied by the impurity. A sublattice is a lattice occupied by a single type of atom. In CdTe the cadmium atoms occupy one sublattice, and the tellurium atoms occupy another sublattice. The superposition of the two sublattices forms the zinc blend crystal structure of CdTe. In type-I the donor and acceptor occupy the same sublattice, and in type-II they occupy opposite sublattices.¹⁶

5. Phonon Replicas

Phonon replicas are a spectral feature produced by the interaction of emitted photons with phonons during the transition. In the recombination process a phonon can be either produced or annihilated as long as energy is conserved. Thus, the energy of the peak due to a transition with phonon

interaction changes by the amount of the phonon energy. There are often multi-phonon interactions that produce multiple peaks. The energy of an LO-phonon is 21.5 meV.¹

C. Typical Photoluminescent Spectra

In photoluminescence a light beam, often from a laser, strikes the material and excites the electrons in it. The photons from the laser are absorbed by the sample, and electron-hole pairs are created. These pairs then recombine and emit other photons of various energies. These photons are collected and separated into different energies, and the number at each energy is recorded. The intensity of the relative peaks in the photoluminescent spectrum indicates which energies of emitted photons are more prominent.

Figure 4 shows a typical spectrum for pure CdTe at 12 K. Since the band gap at 1.8 K is 1.6 eV, the peaks are all at lower energies (longer wavelengths) than this value. Band-to-band recombinations are evident only in very pure samples at 1.6 eV, the band gap energy (not shown in this figure).¹⁷ The exciton region is the region of energies between the band gap (1.61 eV) and 1.58 eV. The shoulder at 1.5955 eV (777.2 nm) is associated with the recombination of free excitons in their ground state. The recombination of free excitons in their first excited state can barely be detected at approximately 1.603 eV (774 nm). The peaks at 1.5932 eV (778.3 nm) and 1.5907 eV (779.5 nm) are associated with the

recombination of excitons bound to neutral donors and to neutral acceptors, respectively.

The peak at 1.55 eV is actually a doublet. (The doublet is not resolved in Fig. 4.) The doublet peaks at 1.5588 eV (795.5 nm) and 1.5539 eV (798 nm) are associated with the F-A and D-A transitions, respectively. This doublet is replicated at approximately 21.5 meV below the doublet. This energy is associated with the energy of an LO-phonon. The peaks at approximately 1.53 eV (810 nm) and 1.51 eV (820 nm) are associated with the first- and second-order phonon replicas of the F-A and D-A transitions.¹ The peak at approximately 1.43 eV (870 nm) is associated with phonon replicas riding on a broad defect band. The zero-phonon line is at 1.45 eV, and the other phonon peaks are separated by multiples of 21 meV from this line. As defects, impurities, and dopants are increased in a material, the overall intensity of the defect band upon which the phonon replicas ride increases until finally the phonon replicas become difficult to resolve.¹⁸ In my data there is also a peak in the infrared region at approximately 1150 nm. This peak--which I will call the mid-gap peak--has not been extensively studied previously. My research has focused on the phonon replica/defect band and the mid-gap peak.

III. DESCRIPTION OF EXPERIMENT

The apparatus for this experiment at the physics department of the University of Utah was a low-temperature photoluminescence system with argon-ion and helium-neon lasers to excite the samples (Fig. 1). The power of the laser varied from 1 mW to 100 mW. The laser beam traveled through a high-pass filter to remove plasma lines. After the beam passed through a chopper (usually run at 50 Hz), two mirrors directed it onto the sample. A cylindrical lens focused the beam down on the sample. A cryochamber with a liquid helium reservoir surrounding the chamber cooled the sample to 4-5 kelvin. A needle valve controlled the temperature by allowing the helium into the sample chamber through the valve. Pumping on the sample chamber could lower the sample temperature to approximately 2 kelvin. The laser illuminated the sample at approximately 45 degrees, and the emitted light was collected at 90 degrees from the incident beam. The emitted light passed through two lenses and a 710 nm low-pass filter before entering a monochromator. The filter cut out any laser light reflected off the sample. A germanium pin detector coupled to a lock-in amplifier and computer detected the light. Figure 1 is a schematic drawing of my

Figure 1: Experimental Setup

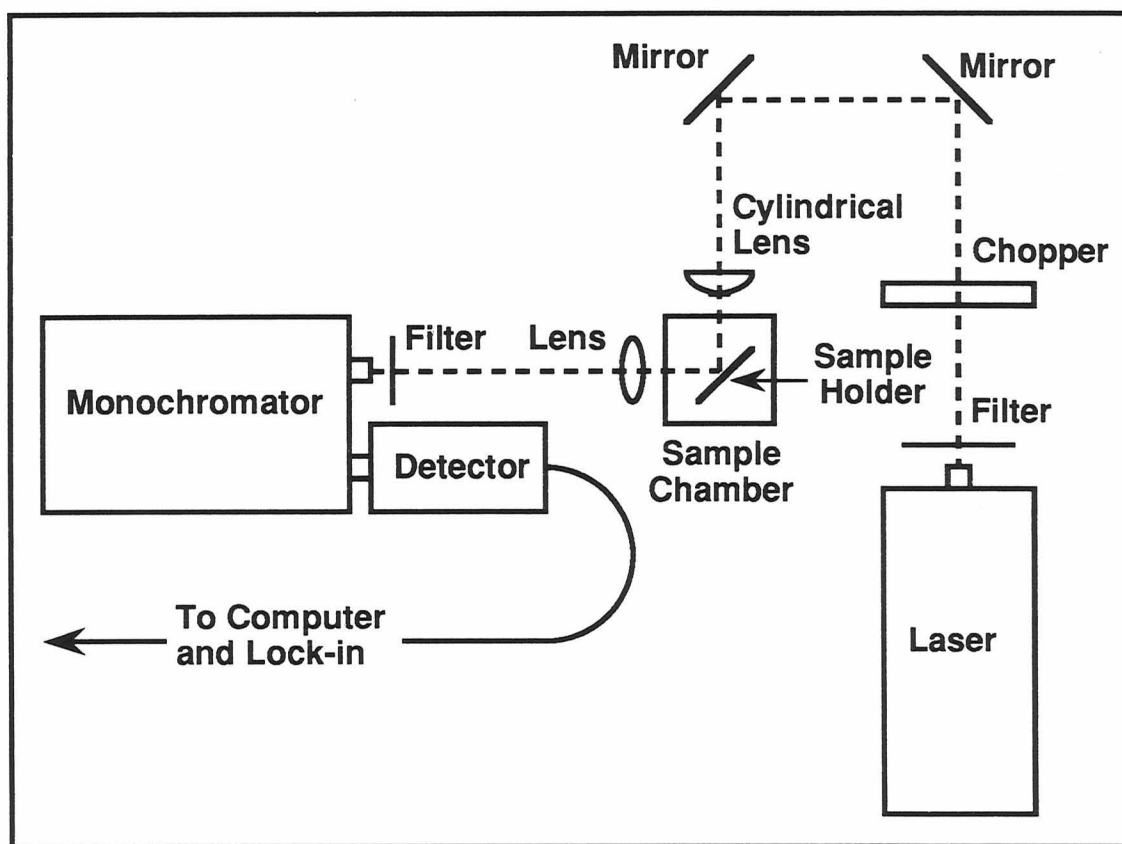


Fig. 1. Experimental setup

experimental setup. I investigated the luminescence in the near-infrared/infrared region (~600 to 1800 nm).

The $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ samples were prepared by Dr. Worth P. Allred at Galtech Semiconductor Materials Inc. (Mount Pleasant, Utah). He grew them using a modified Bridgman method. This company is a source of high-quality crystalline materials. The nominal composition of the $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ samples varied from $x = 0$ to $x = 0.2$. The composition was checked by the position of the main exciton line in the photoluminescence spectrum and by x-ray fluorescence using a scanning electron microscope.

Many different sample preparations were used including cleaving, etching, polishing, annealing, and other surface preparations. Samples were etched 60 seconds in 1% Br-Methanol, and then 120 seconds in 3.5 mol KOH. Polished samples were polished by Worth Allred at Galtech. Pure CdTe samples along with nominal 4% zinc (actually 3%), nominal 8% zinc (actually 3%) and nominal 20% zinc (actually 9%) were studied. Both sides of thick film samples were examined because the zinc content is different on the side of the film towards the substrate and the side where the growth takes place. The films were prepared by closed vapor transport (CSVT). Two bulk, pure CdTe samples with impurities, labelled Raytheon sample and high-conductivity sample, were also studied.

IV. RESULTS

A. Background

Data were taken on photoluminescence apparatus in room B-20 at the Department of Physics of the University of Utah. After checking the data with the literature for CdTe and related II-VI semiconductors, I proceeded to look specifically at the spectrum of $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ in the near-gap and mid-gap regions. A germanium (pin) detector was used. With this detector, data can be obtained for these materials in the mid-gap region, which has not been studied extensively. The data show the expected shift of the spectrum to higher energy (lower wavelength) for samples of higher zinc concentrations. The spectra also show the phonon replicas that have been observed in studies of other semiconductors but have not been well-characterized for CdTe and mixed crystals. Since I used a germanium (pin) detector, the data show higher peaks in the infrared than the literature and relatively lower peaks in the lower wavelength region. The spectral response of the monochromator-detector combination is shown in figure 2. In some cases I have normalized the data using the spectral response curve in figure 2. It does not make a significant difference except in the mid-gap region. I have also included a spectrum taken using a S-20

Figure 2:
Monochromator/Detector Response Curve

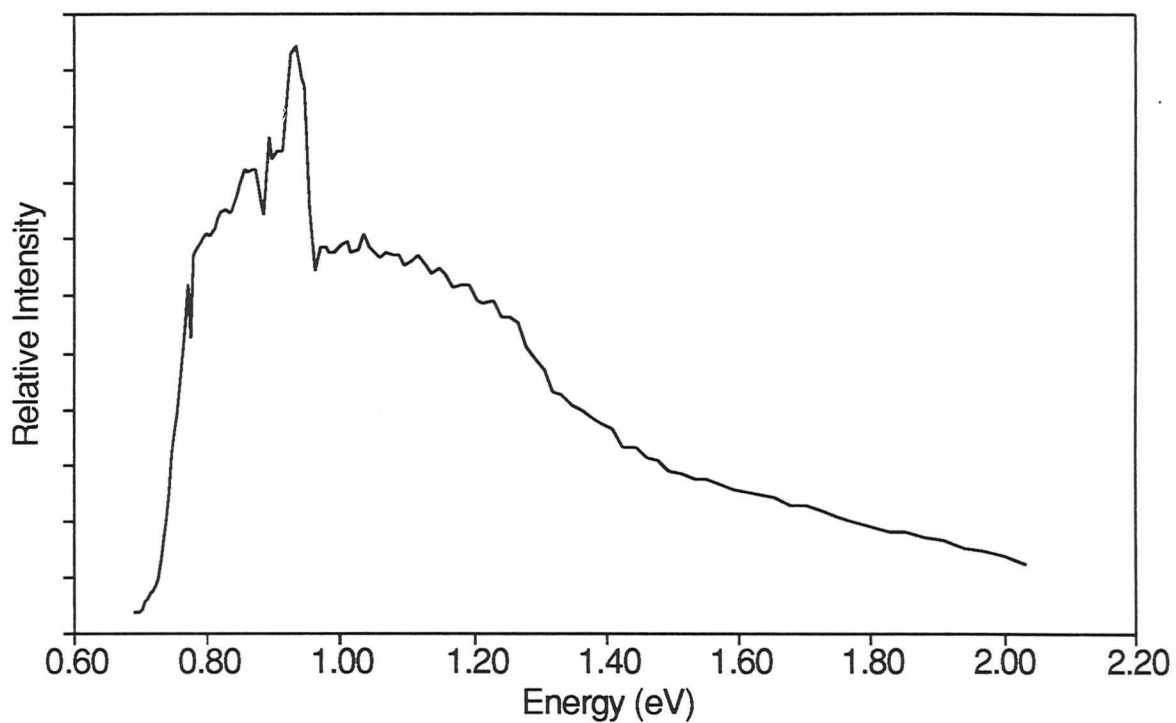


Fig. 2. The spectral response of the monochromator-detector combination. This curve was taken by Matt Delong on the University of Utah photoluminescence system.

photomultiplier-tube detector to show the comparison between my data and previous data taken by others (Fig. 3).

The spectra show differences in relative peak heights in different samples. Absolute peak intensity depends on the positioning of the laser on each sample as well as other factors, so it is difficult to make exact comparison in absolute intensity from sample to sample. The relative differences are probably due to variations in impurity and defect content and differences in composition due to changes in zinc concentration between samples. At lower energy, approximately 1.08 eV (1150 nm), there is also a peak that is not studied in the literature. I will refer to this peak as the mid-gap peak. My research has focused on the phonon replica/defect band and the mid-gap peak. I will begin by describing the typical spectrum for pure CdTe and then tell how other spectra differ as zinc is incorporated or the samples are treated in other ways.

B. Pure CdTe

Pure CdTe has a band gap of 1.61 eV (771 nm) at 1.8 K. Figure 4 shows a typical spectrum for pure single-crystal CdTe at 5 K. This spectrum was chosen because it clearly shows the phonon replicas (from 1.45 eV to 1.35 eV); spectra using a higher laser power show a relatively smaller signal for these features. In my data for pure CdTe the excitons are at 1.591 eV (780 nm) and 1.585 eV (783 nm). The donor-acceptor peaks are lower in energy than the excitons. There are three peaks that are each

Figure 3: S-20 vs. Germanium Detector

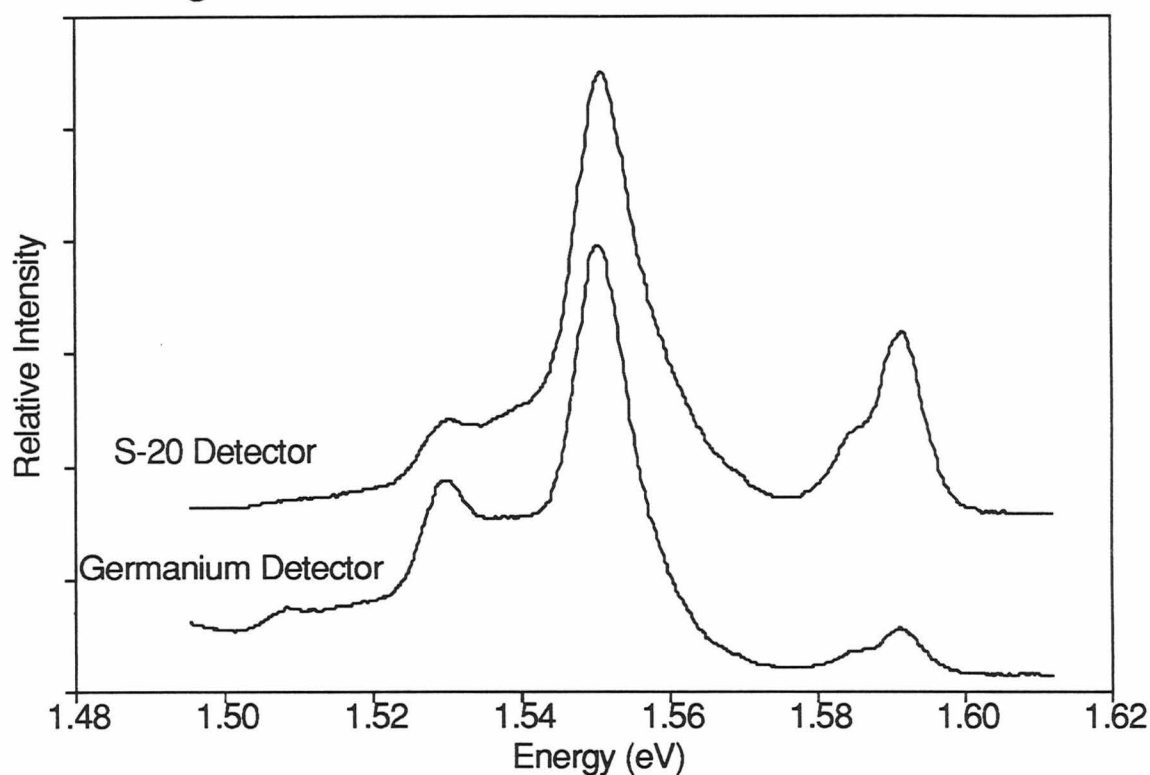


Fig. 3. Pure CdTe spectra taken with an S-20 detector and a germanium pin detector. This comparison is useful when comparing my data to other data in the literature where an S-20 detector is often used. The S-20 has a higher spectral response in the visible (higher energy) and dies out over this energy range (1.50 eV to 1.60 eV) while the germanium pin detector has a higher response in the near infrared and increases in sensitivity over this energy range. Data were taken at 5 K and 10 mW laser power.

Figure 4: Typical Pure CdTe Spectrum

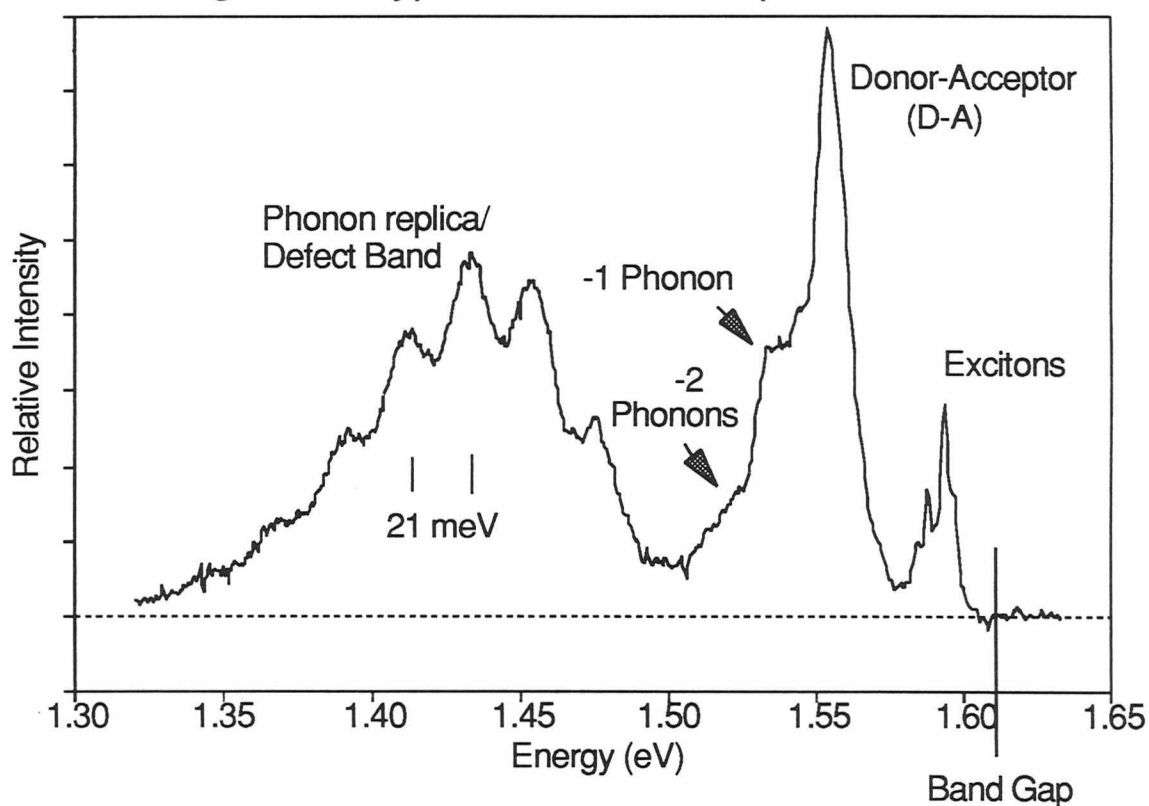


Fig. 4. A typical pure CdTe spectrum. This spectrum was chosen because it clearly shows the phonon replicas. Spectra taken using a higher laser power show a relatively smaller signal for these features. These data were taken at 5 K and 1 mW laser power.

separated by approximately 21 meV (11 nm). These peaks are not always well defined but instead can look like shoulders on the main peak as in Fig. 4. (See Fig. 7A pure CdTe). The largest peak is at the energy associated with the donor-acceptor level, 1.55 eV (800 nm) for pure CdTe. There are also two phonon replicas of this main peak that are 21 meV (12 nm) and 42 meV (23 nm) toward lower energy with respect to the main peak. These correspond to the creation of one and two phonons, respectively, in the recombination process. At high power (see Fig. 7A) these two peaks are usually about 25 percent and 10 percent of the intensity of the main peak. The main donor-acceptor peaks are about four times as intense as the excitons, the phonon replicas, and the mid-gap peak, all of which are at about the same amplitude, depending on the power of the laser. González et. al. contend that this peak is actually a doublet. I have not taken high-resolution data to see the doublet because this has not been the emphasis in my study. González refers to the two peaks as F-A and D-A and places them at 795.5 nm and 798 nm, respectively, which represents a shift of about 5 nm to lower wavelength (10 eV) when compared with my data. Part of this discrepancy could be due to wavelength calibrations. Both peaks are then replicated approximately 21.5 meV (10 nm) below the first peak.¹

The next feature, termed the defect band, begins about 80 meV lower in energy than the main donor-acceptor peak. It starts at 1.477 eV, is centered at about 1.40 eV, is 140 meV wide, and consists of at least seven separate peaks superimposed on a broader peak. Each smaller peak is

separated by about 21 meV (1.3 nm), the energy of a LO-phonon. (Fig. 4 was chosen to emphasize this peak.)

Last of all, there is a wide peak further into the infrared. This mid-gap peak is one of the focuses of my research. It is centered at 1.08 eV (1150 nm) and is about 157 meV (175 nm) wide at half maximum (Fig. 5). Some samples show a shoulder on the longer wavelength side of this peak. This shoulder is probably due to the monochromator-detector response. When normalized by the response curve, it effectively disappears (Fig. 6).

C. Effect of Substituting Zinc for Cadmium

As was mentioned, by replacing cadmium with varying amounts of zinc, the band gap energy can be tailored from 1.61 eV, the low-temperature band gap of pure CdTe, to 2.4 eV, the low-temperature band gap of pure ZnTe. The nominal composition of my samples is pure CdTe, 4% zinc, 8% zinc, and 20% zinc. Recent electron-microprobe x-ray fluorescence indicates that the actual zinc composition of the 4% and 8% samples is 3% zinc and the 20% sample is actually 9% zinc. The band gap energies for $x = 0.03$ (3% zinc), and $x = 0.09$ (9% zinc) are approximately 1.625 eV and 1.65 eV, respectively.¹⁹ I have studied the changes in the spectra at 5 K with these different concentrations of zinc in $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ (Fig. 7A). At first the intensity of the exciton relative to the donor-acceptor peak increases with increasing zinc. Although the zinc composition of the nominal 4% and 8% samples is approximately the same, the spectra are

Figure 5: Mid-Gap Peak

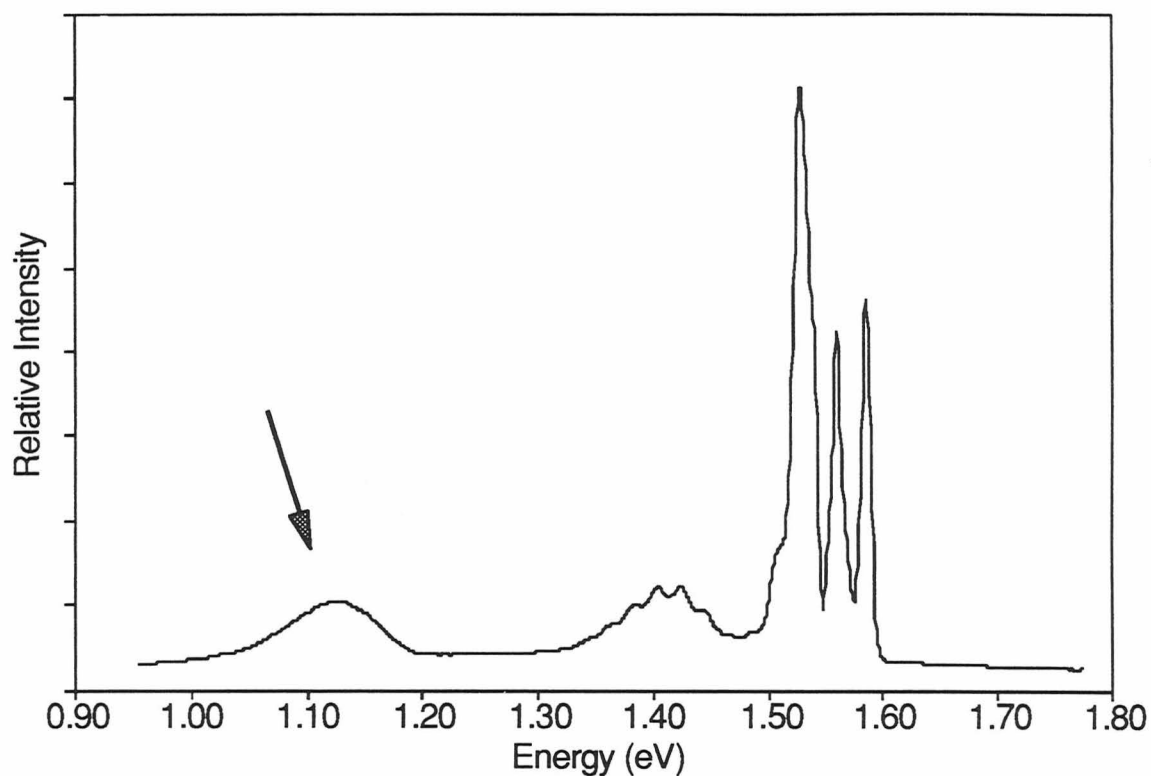


Fig. 5. This peak in the mid-gap region has not been studied in the literature. This spectrum of pure CdTe was taken at 80 mW laser power. The relative intensity of the mid-gap peak is higher than in spectra taken at lower laser powers.

Figure 6: Normalized Mid-Gap Peak

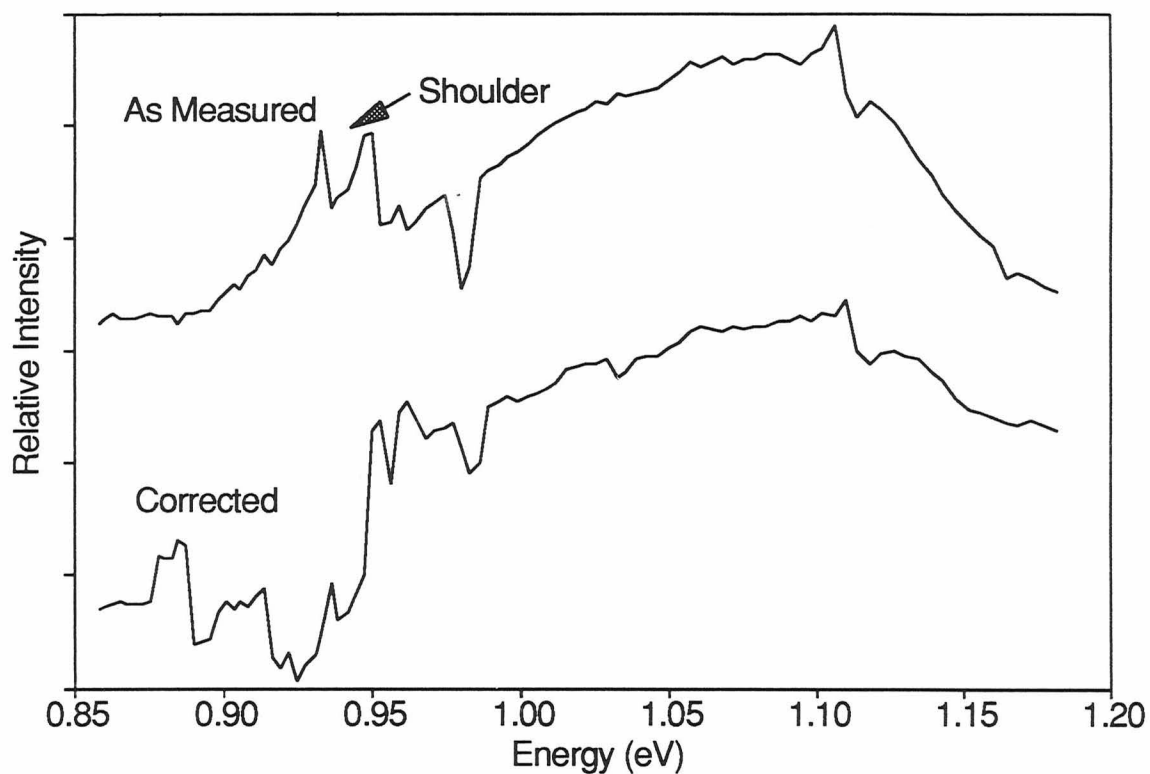


Fig. 6. Normalized mid-gap peak. Some samples show a shoulder on the lower energy side of the mid-gap peak. This shoulder is probably due to the monochromator-detector response. When normalized by the response curve, it effectively disappears.

Figure 7A: Varied Zinc Content

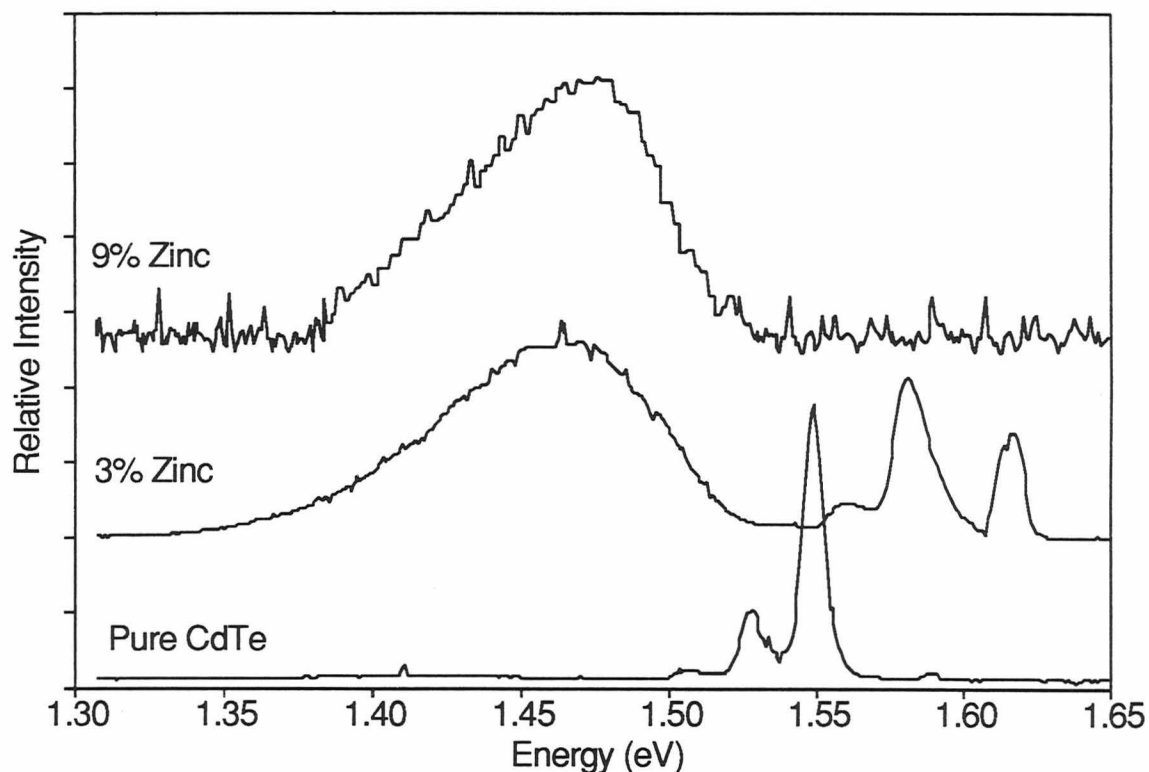


Fig. 7A. Varying the zinc content in $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ changes the spectrum. Note that the features at higher energies than 1.50 eV decrease in intensity and shift toward higher energy with more zinc, but the peak at lower energy increases in intensity and shifts in the opposite direction. All measurements were made at 5 K. The pure CdTe and the 3% sample spectra were taken using 10 mW laser power but the 9% sample was taken using 1 mW laser power which explains the difference in signal-to-noise ratio.

different (Fig. 7B). For $x = 0.04$ (nominal composition) the exciton peak intensity is approximately 75% of that of the donor-acceptor peak. In the spectrum of the nominal $x = 0.08$ sample, the excitons become small and cannot be seen at higher concentrations of zinc. This probably results from the increase in disorder and impurities in the 8% samples due to the process used in trying to increase the zinc content. The excitons for $x = 0.03$ (actual composition) are shifted from 1.596 eV (777 nm) in pure CdTe to 1.616 eV, a shift of 20 meV (13 nm). The excitons for $x = 0.09$ nm are not seen in my data but the expected position is about 1.63 eV, a shift of 44 meV from pure CdTe. This shift is the same as that of the band gap of the material.

Like the excitons, the donor-acceptor peaks shift to higher energy (lower wavelength) when zinc content is increased--from 1.55 eV in pure CdTe to 1.58 eV [a shift of approximately 15 nm (to 786 nm)] for $x = 0.03$. The peaks also decrease in intensity with the increase of zinc but not as fast as the excitons. In 9% zinc samples (actual composition) the donor-acceptor peaks were not detectable (Fig. 7A). The donor-acceptor peaks in the nominal 8% sample were considerably smaller than in the 4% nominal sample even though the zinc composition is the same.

Three changes are noteworthy with respect to the phonon replica/defect band. First, the intensity increases as the percent of zinc increases. In pure CdTe this peak is barely noticeable, but in 9% zinc samples this band is the only feature visible. Second, the individual

Figure 7B: Nominal 4% vs Nominal 8%

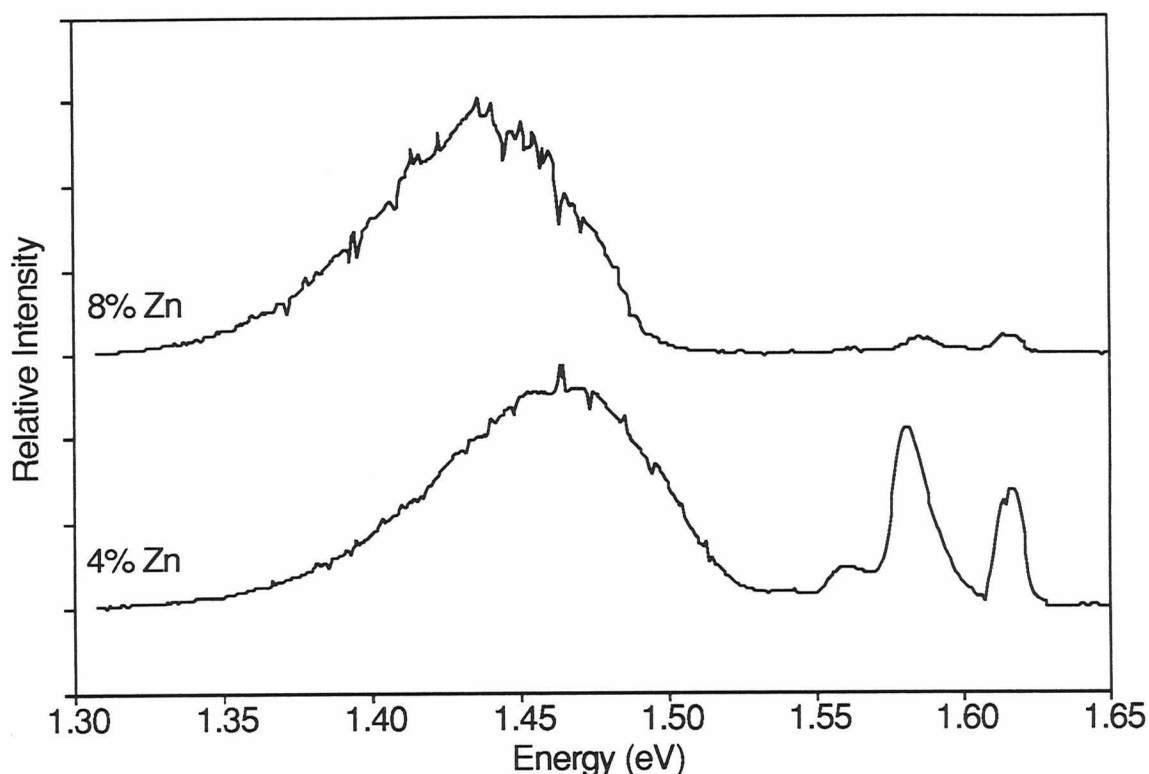


Fig. 7B. Although these were nominal 4% and nominal 8% zinc samples, electron microprobe analysis shows that they are actually both about 3% zinc samples. Yet the spectra are notably different. The exciton and donor-acceptor peaks in the 8% sample are considerably less intense than in the 4% sample. Also the phonon replica/defect band is shifted toward lower energy in the 8% sample. Although the zinc composition is the same, the method of trying to get a 8% sample causes increased impurities or defects in the sample. Thus there is a decrease in the relative intensity of the exciton and donor-acceptor peaks. The shift in the phonon peak/defect band is also possibly do to impurities and defects.

phonon replica peaks become hard to distinguish as the intensity of the peak increases, that is, as the zinc increases. This is due to the replacement of cadmium by zinc which is a much lighter atom. This reduces the symmetry of the crystal, thus, the phonon modes are no longer well-defined. Impurities also have this effect. Third, the phonon replica/defect band does not shift to higher energy with increasing zinc content the way excitons and donor-acceptor peaks do. Therefore, there is a larger separation between the donor-acceptor peaks and the phonon replicas in samples containing more zinc, but the separation is not consistent with the change in zinc content. Although the actual composition is the same in the nominal 4% and 8% samples, the space between the D-A and the phonons in the nominal 8% zinc samples is about 16 meV (10 nm) more than the space between these peaks in the nominal 4% samples. This shows a difference in the position of the phonon replica/defect band due to the sample preparation and not to actual zinc content (Fig. 7B). This result is due either to a shift of the defect band, to the shifting of the zero phonon peak to lower energy, or to the enhancing of replicas produced by the interaction of different multi-phonons in the transition so the center of the peak shifts to lower energy.

These three effects have been seen by others in CdTe samples doped with In (Fig. 8).²⁰ Although replacing cadmium with zinc does not make an n-type material as does doping with indium, the effect on the phonon replica/defect band seems to be similar; a key difference is that many times

Figure 8: Spectra Containing Indium

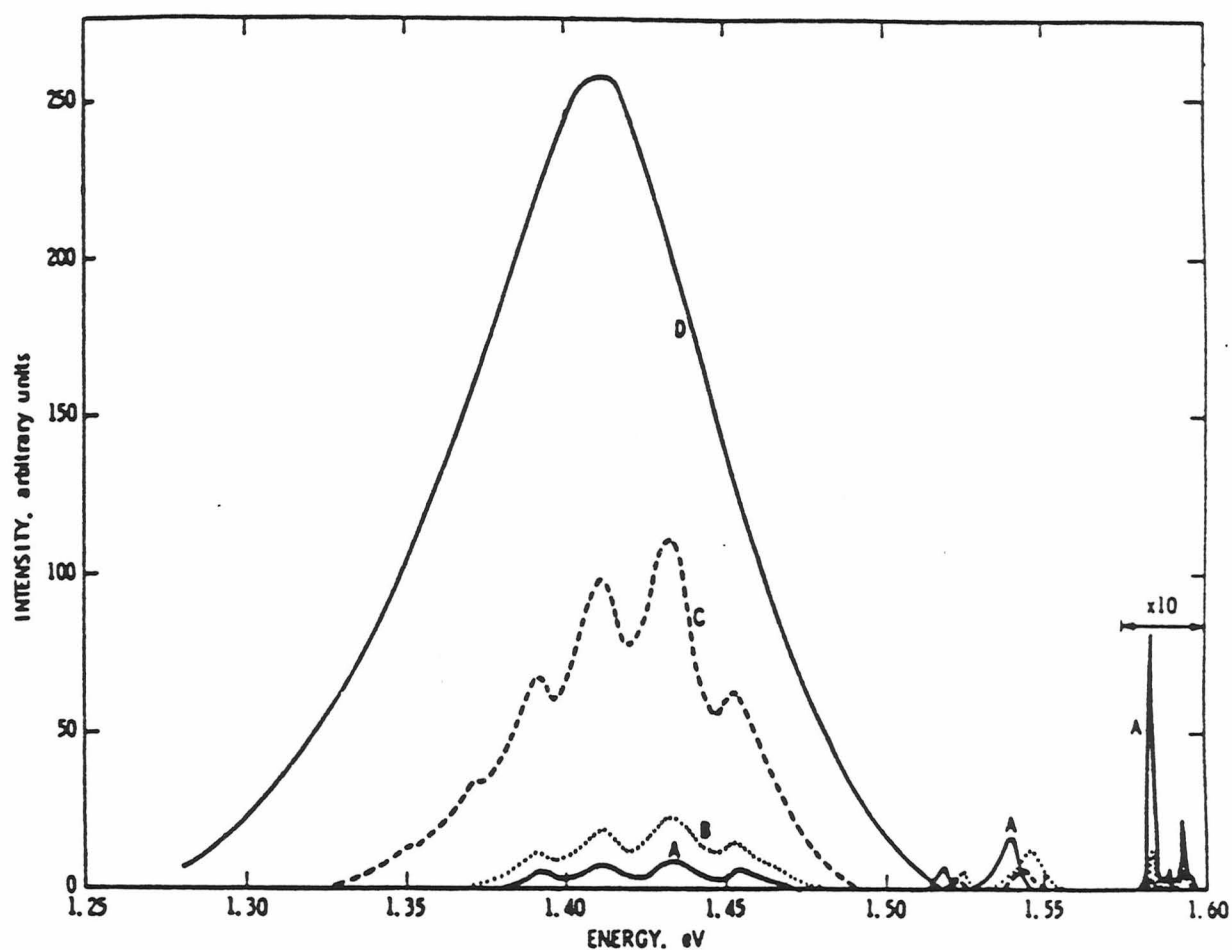


Fig. 8. Photoluminescence spectra of CdTe containing (A) $3 \times 10^{15} \text{ cm}^{-3}$, (B) 10^{16} cm^{-3} , (C) 10^{17} cm^{-3} , and (D) 10^{18} cm^{-3} of In. The same effect is noted when zinc is added to CdTe. Although replacing cadmium with zinc does not make an n-type material as does doping with indium, the effect on the phonon replica/defect band seems to be similar though much more zinc is required to produce the same magnitude of effect. Data were taken at 4.2 K by Barnes and Zanio.²⁵

as much zinc as indium is required to produce the same magnitude of effect. Also the atomic weight of indium is much closer to cadmium than zinc is to cadmium. Thus, indium does not affect the phonons in the crystal in the same way as zinc.

The mid-gap peak may also shift in the opposite direction to the excitons and donor-acceptor peaks, but it does not shift the same amount as the defect band. I do not show a figure because the peak is broad and the effect is slight. This shift does not seem to be the same as that of the phonon replicas/defect band since in some samples of identical composition the two peaks do not have the same separation. This shift does not seem directly correlated to zinc content since different samples with similar zinc content shift differently. This peak is usually, but not always, more intense in samples with more zinc. Thus, its intensity may not be connected directly to the zinc content of the sample but more possibly to defects and/or impurities introduced as more zinc is added. If the peak were due to impurities introduced into the crystal due to the addition of zinc, it should increase linearly with zinc concentration. Since this is not the case, this peak is probably due to a defect in the crystal or to an impurity from another source.

D. Temperature Effects

I collected and examined the spectra of pure CdTe as a function of temperature from 2 K to 50 K. Studies of the temperature dependence of

spectra have proved useful in identifying peaks. Shallow levels are easily ionized at higher temperatures while peaks associated with deeper levels can be seen at higher temperatures. As the temperature increased, the exciton and the donor-acceptor peaks decreased. At 50 K only the phonon replicas showed up in the spectra (Fig. 9). In general, the free exciton line disappears first, followed by the bound excitons, which disappear more slowly. The phonon replica/defect band was only slightly affected by temperature, which suggests that it is connected with only deep level transitions. The individual phonon replica peaks are, however, affected by temperature. They become indistinguishable at about 30 K, perhaps because the zero phonon line is ionized at higher temperatures. The PL intensity as a whole decreases because the non-radiative recombination process becomes increasingly important as the temperature increases, thus radiative recombination decreases. No signal can be detected at room temperature.

E. Surface Preparations

Since the effective penetration depth of the laser light in CdTe is only a few tenths of a micron, various surface preparations can help understand whether features in the spectra originate in the bulk or in the surface of the sample. When the surface of the samples was etched by placing them for one minute in 1% Br-methanol and then for two minutes in 3.5 molar KOH, the exciton peaks and the donor-acceptor peaks, especially, were cleaner

Figure 9: Temperature Dependence

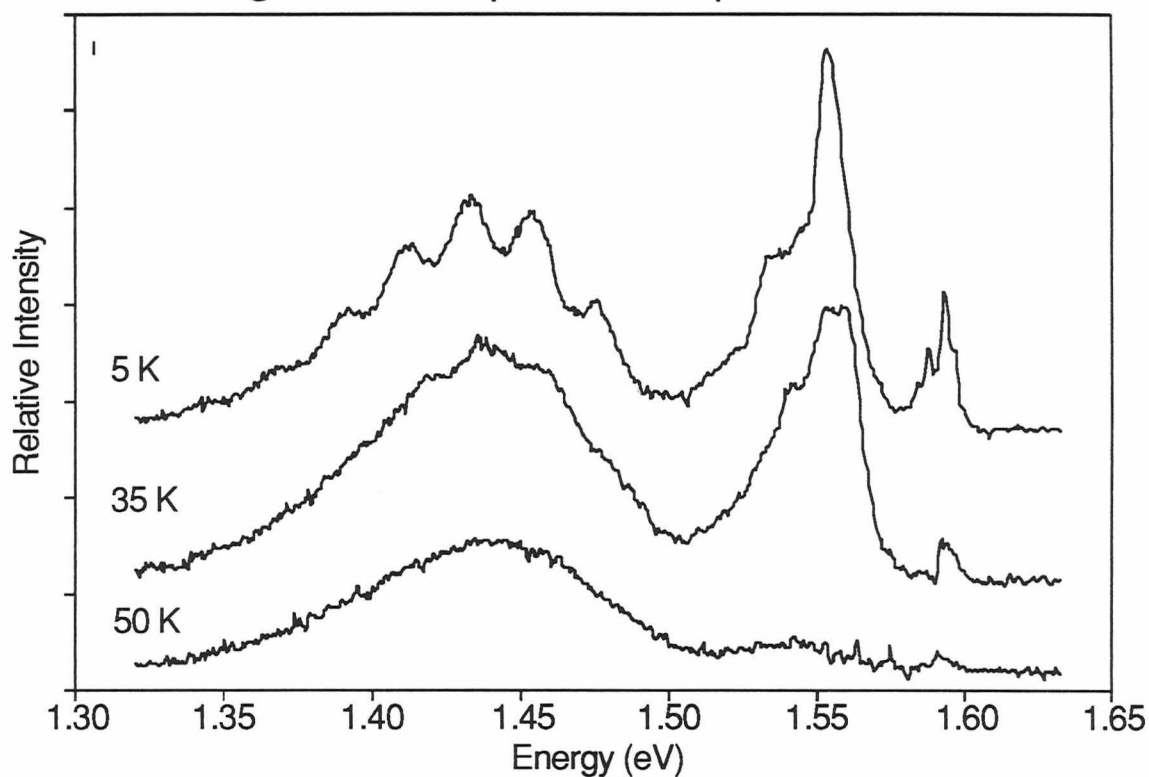


Fig. 9. Temperature dependence of pure CdTe. The intensities of the features at the higher energies (excitons and donor-acceptor peaks) decrease with increasing temperature while the intensity of the lower energy peak (phonon replica/defect band) does not change significantly. The main change in the lower energy peak is that the individual phonon replica features become indistinguishable.

and more intense (Fig. 10). In general, the signal as a whole is more intense compared to the noise in an etched sample. Treating the surface can reduce the rate of surface recombination and thus increase the carrier lifetime and enhance the emission processes I am studying.

Polished samples were studied because polishing can affect more than just the surface of the sample. The spectrum of a polished surface of a sample is different from that of a cleaved surface. The polished sample has a larger phonon replica/defect band than that of a newly cleaved surface. The defect bands in the spectra of a polished sample, however, were comparable in intensity to those of a surface that was cleaved more than a month earlier. The old cleaved surface, however, showed donor-acceptor peaks that were approximately half the size of the donor-acceptor peaks in the newly cleaved surface and the polished surface. Thus sitting in air either increases the defect band or decreases the excitons and donor-acceptor peaks (Fig. 11A). This effects suggests that the intensity of the defect band is affected by surface impurities. I cannot conclude from these data, however, that the phonon replica/defect band originates from surface qualities of the sample. It could be due to bulk characteristics and still be affected by changes on the surface.

In the polished samples, the mid-gap peak was generally larger than in the cleaved samples (Fig. 11B). This peak is seen in the cleaved samples but is so small it is almost insignificant. Polishing induces impurities and defects which are not only confined to the surface as are the impurities in

Figure 10: Etched vs. As-Prepared

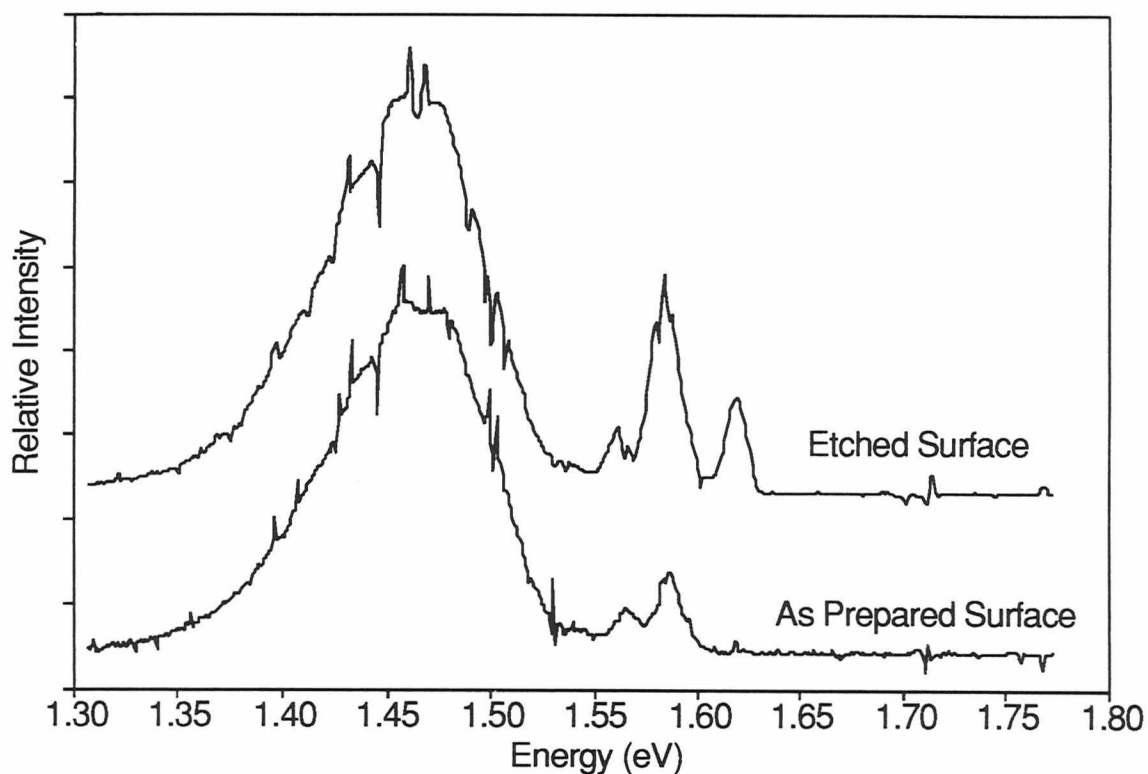


Fig. 10. Spectra for a sample with an etched surface and for the same sample with the surface as prepared. The surface of the samples was etched by placing it for one minute in bromine methanol and then for two minutes in 3.5 molar KOH. The exciton peaks and the donor-acceptor peaks, especially, are cleaner and more intense in the etched sample.

Figure 11A: Cleaved vs. Polished

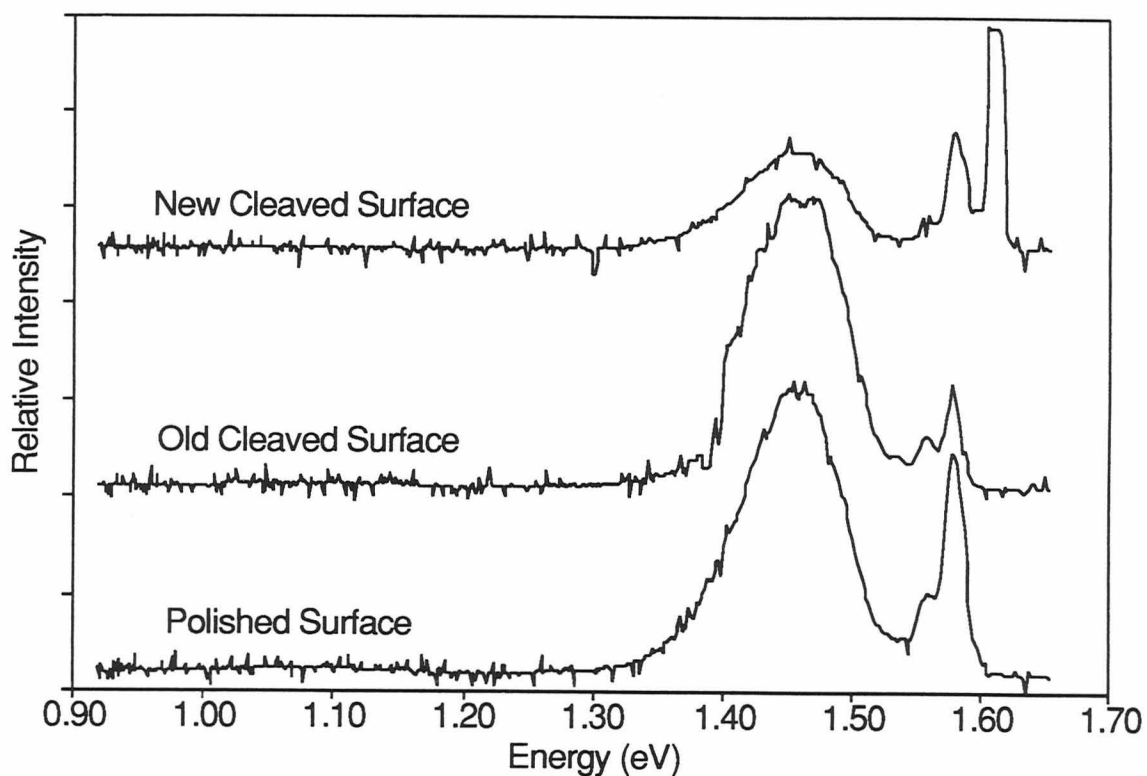


Fig. 11A. Spectra from a sample with a polished surface compared to those with cleaved surfaces. The polished surface and the old cleaved surface (cleaved about a month before measurements were made) have a larger phonon replica/defect band than the newly cleaved sample. This result suggests that the intensity of the defect band is affected by surface impurities.

Figure 11B: Mid-Gap Peak Magnified x40

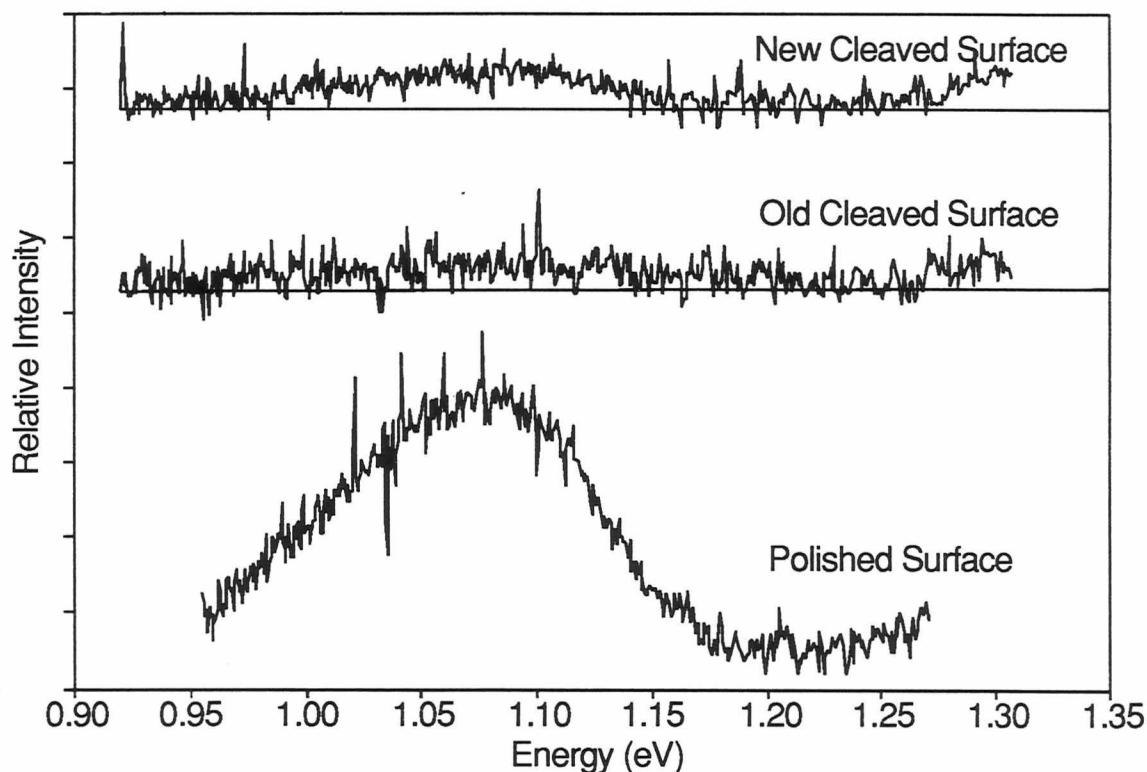


Fig. 11B. A magnified (400%) spectrum of the mid-gap peak from figure 11A. Although the figure is not visible in figure 11A, magnification shows how much larger the mid-gap peak is in the spectrum for the polished surface than in those of the cleaved surfaces. This peak is not affected by the exposure of the cleaved surface to air. Data were taken with 1 mW laser power. In spectra taken with higher laser power, the mid-gap peak is more intense relative to the rest of the spectrum (see Fig. 5).

an old-cleaved surface. It is these impurities and defects that seem to contribute to the mid-gap peak.

F. Evaporated Materials

I also looked at two sides of approximately 100-micron thick film samples. They possess a smooth and a rough side. The smooth side is the side that was against the substrate during deposition and thus is the first material deposited while the rough side was the last material deposited. The smooth and rough sides of the samples have different zinc composition due to the method of preparation. The excitons and donor-acceptor peaks of the smooth side of a nominal 4% zinc sample are shifted (Fig. 12) from a peak maximum of 1.624 eV on the rough side to 1.611 eV for the smooth side of the sample, about 13 meV toward lower energy (7 nm to longer wavelength). This result suggests that the rough side of the samples is rich in zinc and the smooth side is relatively zinc poor. This condition is what is expected since zinc is less volatile than cadmium, and it therefore evaporates from the source preferentially toward the end of the deposition.

The high-energy side of the phonon replica/defect band is at approximately 1.567 eV on both the smooth and rough sides of this sample. This is a shift of about 67 meV toward higher energy than the start of this peak in the typical pure CdTe sample. There is more space, 57 meV compared to 44 meV, between the D-A peaks and the phonon replicas on the smooth side of the sample than on the rough side. The phonon

Figure 12: Rough vs. Smooth Surfaces

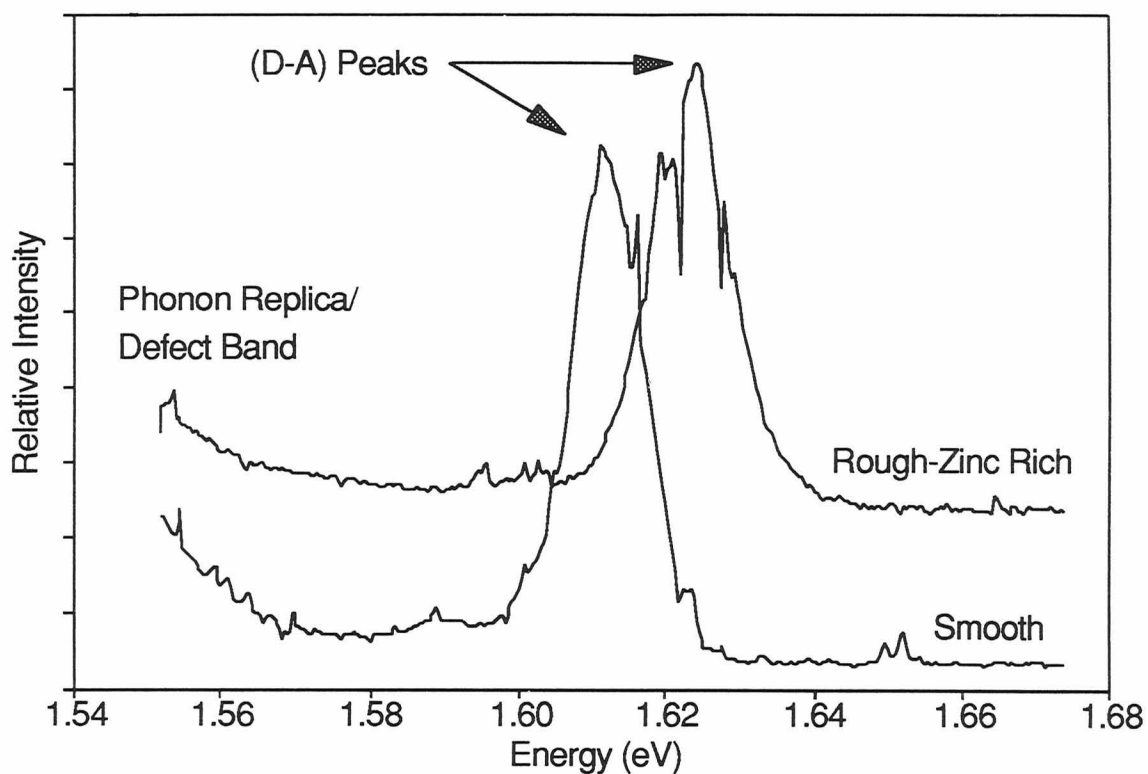


Fig. 12. Spectra of a 4% zinc film sample from the rough surface, the side of the sample where growth is occurring, compared to the smooth surface, the surface which is against the substrate, of the same sample. The position of the donor-acceptor peaks is different due to the slight difference in zinc content, but the phonon replicas begin at the same energy. The rough side of the sample is rich in zinc.

replica/defect band is not as sensitive to small changes in zinc as the excitons and donor-acceptor peaks. This fact suggests that the zero phonon line (the energy of the transition that is interacting with the phonons to create the replicas seen in the phonon replica/defect band) is not connected to the exciton or donor-acceptor transitions. Although the position of the defect band should be affected by the band gap of the material, it does not seem to be directly connected to zinc content; it thus shifts independent of the band gap of the material.

It is more difficult to detect shifts in the mid-gap peak because it is broad and not well defined. Although there are some slight differences between the rough and the smooth sides of the same evaporated film samples, the shifts are small, and the data do not clearly point to a shift either way. This indicates that when comparing samples of approximately equal zinc compositions, there is no consistent movement of the mid-gap peak.

G. Intentional Modifications of the Sample Surfaces

To further understand which elements of the spectra are surface effects and which are due to bulk characteristics of the sample, surface defects were induced. Surface preparation techniques suggested in the literature were applied.²¹ The only effect of this on the spectra was to decrease the relative intensity of the phonon replica peaks. This reduction could result from a decrease in defects due to the surface preparations.

The relative magnitude and position of the peak in the mid-gap region did not significantly change.

H. Different Laser Wavelengths

To look at various depths in the materials, two different laser wavelengths, 632.8 nm (red helium neon laser) and 488.0 nm (blue-green argon-ion laser), were used. Since the red light has a longer wavelength, the penetration depth is greater; thus, the spectra will show more of the bulk characteristics than that of the shorter-wavelength laser. There was no significant difference in the spectra. This implies that the peaks in the spectra are due to bulk (at least as deep in the samples as the 632.8 nm laser penetrates) effects and not just to surface effects. The light penetrates further into the samples with higher zinc concentration because of the increased band gap as zinc replaces cadmium. The penetration depth is determined by the absorption coefficient given in equation (10) on page 5.

I. Annealed Samples

I also examined the effects of annealing samples, which can either heal bulk and surface defects or produce them, depending upon the temperature at which the sample is annealed and how the sample behaves at that temperature. Annealing eliminated the donor-acceptor peaks and decreased the intensity of both excitons and the rest of the signal in pure CdTe and in 3% zinc samples. The excitons can still be observed, but the signal-to-noise ratio is much lower so it is more difficult to detect them.

Annealing also altered the character of the phonon replica/defect band. The spectra show a noisy signal that begins at about the band gap energy and increases to a hump where the phonon replica/defect band usually is and then decreases again. The individual phonon replica peaks cannot be resolved at the laser power used.

The mid-gap peak changes dramatically. It is huge in an annealed sample even when it is very small in the sample before annealing. This result would suggest that it is connected with bulk defects.

J. Samples with Bulk Impurities

I examined two other types of materials--a single-crystal pure CdTe sample labelled Raytheon, which produces high resistive samples when used as a substrate (with cleaved and polished surfaces), and a highly conductive (2 ohm-cm instead of approximately 10^8 ohm-cm) sample of pure CdTe. The Raytheon sample does not contain zinc, but may contain an impurity (most likely lithium). The spectra from both the cleaved and polished surfaces of the Raytheon were quite dissimilar from previous spectra. The main difference between the two surfaces is that the peak at 1.577 eV (33 meV lower in energy than the band gap) in the cleaved-sample spectrum is not in the polished-sample spectrum (Fig. 13). There is also a small peak at about 1.56 eV (50 meV lower in energy than the band gap). These peaks cannot possibly be the usual exciton peaks since they are at lower energies (further from the band gap energy) than any of the exciton

Figure 13: Raytheon Sample

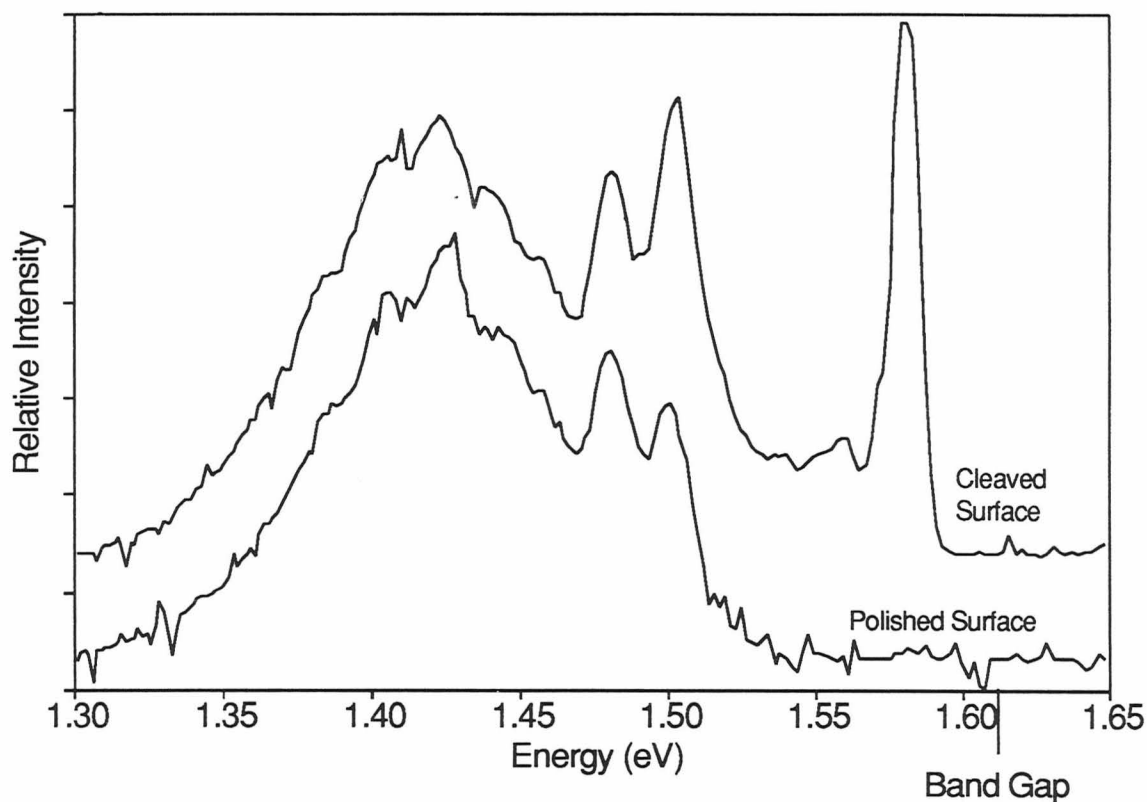


Fig. 13. The spectrum from a sample labelled Raytheon. This sample is pure CdTe but it has an impurity (most possibly lithium) that causes high resistivity when it is used as a substrate. The two peaks at about 1.60 eV are probably part of the phonon replica/defect band even though the relative intensities of the phonon replicas differ from a pure CdTe sample. The width of the phonon replica/defect band is also about 40 meV, the energy of these two extra phonon replicas, greater than in a pure CdTe sample. This spectrum was taken at 4 K and 20 mW laser power.

peaks in other pure CdTe samples. The position of these peaks is actually about the same as that of the donor-acceptor peaks in 4% zinc samples. They may be due to an unknown impurity in the sample. In both samples there are two peaks at 1.501 eV and 1.480 eV that look like they could be the donor-acceptor peaks, but they are red-shifted to enter the range of the phonon replica peaks. Also, they have a separation of about 21 meV, the same separation as the phonon replica peaks. This suggests they are actually part of the phonon replica/defect band. The phonon peaks also have a slightly smaller spacing, approximately 19-20 meV instead of 20-21 meV. In this model there are no excitons in the spectra; thus, all the peaks are associated with the donor-acceptor peaks, the phonon replicas, and the defect band. The difference in this phonon replica/defect band is that the basic shape is not gaussian. Instead, the two higher-energy phonon replicas (at 1.501 eV and 1.480 eV) are more intense than the third (at 1.460 eV), and the intensities of the next three are about the same as those of the first two. There are also more phonon replicas than in other pure CdTe samples. In some samples seven replicas can be detected (Fig. 4), but in this sample there are possibly nine distinguishable replicas. This makes the phonon replica/defect band wider than in other samples. When measured, it is about 190 eV wide as compared to 150 eV. The extra width is about equivalent to the energy of two phonons. This result shows that the relative intensities of different multi-phonon interactions and the number of phonon replica peaks can vary. The defect band could also

affect the intensities, position, and number of phonon replica peaks seen in a spectrum.

In both samples there was a mid-gap peak. In the cleaved sample this peak is slightly more intense than in the polished sample, and it is shifted to slightly higher energy (Fig. 13).

The highly conductive sample is also a pure CdTe sample with no zinc added, but I suspect an n-type impurity that makes it highly conductive--2 ohm-cm conductivity (Fig. 14). The highly conductive sample shows two peaks at 1.576 eV and 1.558 eV (34 meV and 52 meV lower in energy than the band gap). These peaks are at the same position as the higher energy peaks in the Raytheon sample. As in Raytheon, these energies seem too low for exciton peaks, so they are probably donor-acceptor peaks associated with an unknown impurity in the sample. Since their positions are the same as in the Raytheon sample, the impurity is probably the same in both samples. The separation is 18 meV, which is approximately the separation of a donor-acceptor peaks and a phonon replica of that peak. The phonons do not begin until about 60 meV lower energy than those in the Raytheon sample. (The first three phonon replicas are not visible.) There are then six phonon replicas that match the positions and relative intensities of the fourth through the ninth replicas in the Raytheon sample. This makes the energy difference between the donor-acceptor peaks and the phonon replica/defect band larger than in a typical pure CdTe sample. The phonon coupling must be such that the optimum

Figure 14: Highly Conductive Sample

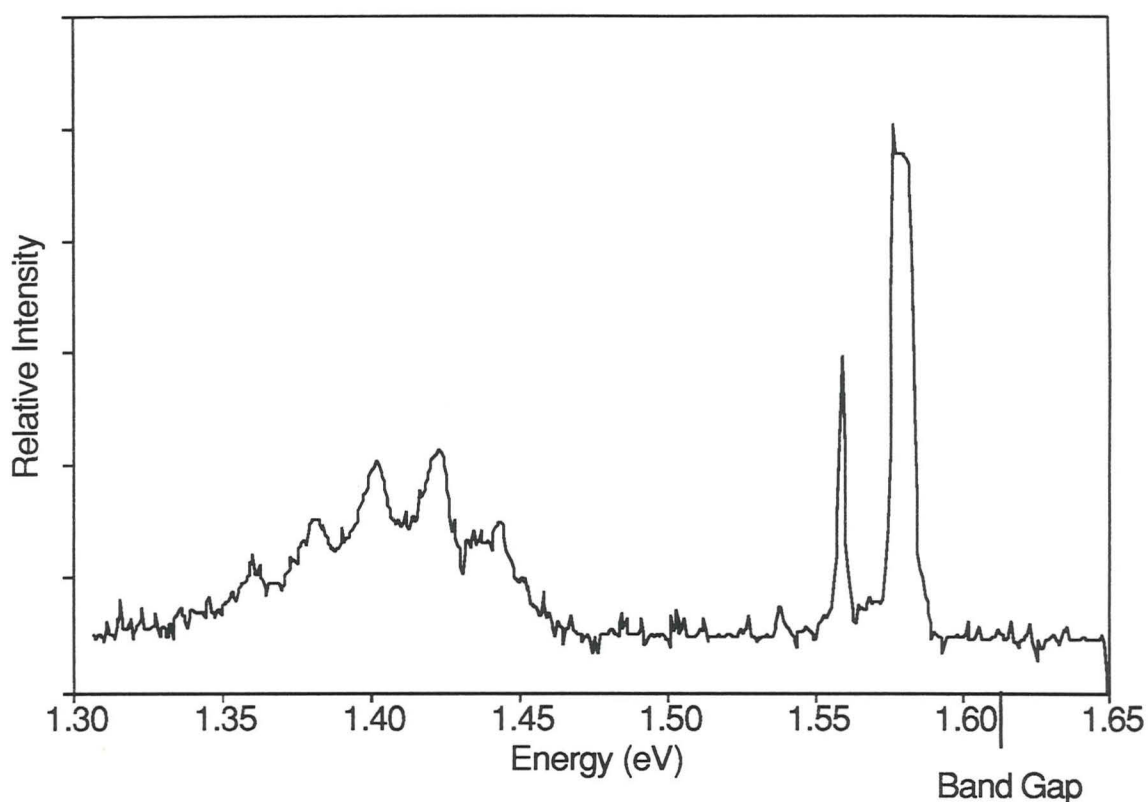


Fig. 14. The spectrum of a highly conductive sample, 2 ohm-cm conductivity compared to the usual 10^8 ohm-cm in a typical CdTe sample. This is a pure CdTe sample with an n-type impurity which makes the sample highly conductive. The phonon replica/defect band matches the lower energy peaks in the Raytheon sample, but the highest energy phonon replica in this sample matches the energy of the fourth highest energy phonon replica in the Raytheon sample. The phonon replica/defect band in this sample is the same width as in a typical CdTe sample, but it is shifted by two phonon replica energies to lower energy. This spectrum was taken at 4 K and 20 mW laser power.

number of phonons produced differs in this sample; thus, the spectrum shows the phonons at lower energies (longer wavelength) are more intense than the ones usually seen. The mid-gap peak is not detectable.

V. DISCUSSION

In order to better describe the phonon replica/defect band and mid-gap peak, I will discuss each separately.

A. Phonon Replica/Defect Band

This feature in the photoluminescence in other materials has often been classified as the defect band. In my research I have found evidence of defects associated with the peak in this region. Surface preparations such as etching and other cleaning methods decrease the intensity of this band relative to the exciton and donor-acceptor peak intensities. Polishing the surface of a newly cleaved sample also heightens the intensity of this peak. A sample that was cleaved more than a month before measurements were taken and was then left in air shows an even larger increase in peak intensity relative to the exciton and donor-acceptor peak intensities than does the polished sample. These data all suggest that surface defects contribute to the intensity of this peak. However, when different laser wavelengths (632.8 nm and 456.9 nm) were used to determine whether this peak was due to surface effects or bulk effect, there was no significant change in the spectra. This result suggests that this defect band is due to bulk (at least as deep as the 632.8 nm laser penetrates) characteristics of the sample although it may also be affected by surface defects.

I also see evidence of phonon replicas superimposed on this defect band. Especially in samples where the intensity of this peak is low, small peaks separated by approximately 20-21 meV are superimposed on this defect peak. These peaks are more distinct in samples with lower zinc content. Zinc decreases the phonons in the crystal since zinc is an element of smaller atomic weight than cadmium, and the lack of symmetry destroys the phonons. Defects would have the same effect on the phonons. This peak does not shift with zinc content as do the excitons and donor-acceptor peaks (with the band gap). In fact the peak shifts differently in the nominal 4% and nominal 8% samples even though they are both actually about 3% samples. The peak shifts toward lower energy in the nominal 4% zinc samples but shifts back toward higher energy in the nominal 8% zinc samples. The position of this peak in the nominal 8% zinc samples is approximately the same as in pure CdTe. This effect suggests that different multi-phonon interactions could be activated in different zinc samples, thus shifting the peak. If the shift of this peak is a multiple of the phonon energy, 21 meV, then this explanation would be most probable. According to my data, this peak in the spectrum of the nominal 4% zinc sample shifts approximately one phonon toward higher energy, and this peak in the 8% sample shifts back approximately one phonon toward lower energy. Because of the indistinctness of the phonons in these samples, the accuracy is not good, so this theory has not been carefully examined.

Another possible interpretation is that the position of the zero phonon line shifts.

Other aspects of the phonon replica/defect band are the dependence of the intensity on sample temperature at the time of measurement and on the power of the laser used to excite the sample. As the sample temperature increases, the amplitude of the peaks in the spectrum decreases, but this peak decreases much more slowly than others (Fig. 9). By 50 K the exciton and donor-acceptor peaks have disappeared, but the intensity of the phonon replica/defect band is approximately the same as at 4 K. As the laser power increases, the intensity of the phonon replica/defect band decreases relative to the excitons and donor-acceptor peaks. When the laser power increases by a factor of approximately ten, the donor-acceptor peak intensity increases from about one-twentieth of the phonon replica/defect band to about one-half of this band. This change could partially account for the large variation in the relative intensity of the exciton and donor-acceptor peaks and this peak in different spectra of similar sample compositions, especially in those of different zinc concentrations.

B. Mid-Gap Peak

The origin of the mid-gap peak is much more difficult to determine. The two parameters I examined were intensity and position of the peak in different samples. In many samples, even with extensive magnification,

effectively no peak appears in the mid-gap region. In other samples, however, there is a peak of the same order of magnitude as other peaks in the spectrum. The peak intensity relative to the rest of the spectrum increases considerably with laser power, especially relative to the phonon replica/defect band. (Compare Fig. 5 taken at 80 mW laser power with Figs. 11A and 11B taken at 20 mW laser power.) There is an increase in peak intensity in a polished surface relative to a cleaved surface, but there is no significant difference between this peak in an old cleaved surface compared with a newly cleaved surface (Fig. 11B). The most significant changes in this peak occur in annealed samples where this peak becomes large even when it was undetectable in the unannealed samples. Annealing can create or heal bulk defects. It can change the relative number and types of defects. These conditions suggests that this peak is due to bulk crystal defects.^{22, 23} There is also a significant mid-gap peak in the Raytheon sample but not in the highly conductive sample.

VI. CONCLUSIONS

I studied $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ by using photoluminescence. I investigated the region from 0.7 eV to 1.8 eV. Because the study of this material is in its infant state, especially in the infrared region, I have detected features in the spectrum that had not been extensively examined in previous research. These characteristics include the phonon replica/defect band at approximately 1.44 eV and the mid-gap peak at about 1.09 eV. I call the peak at 1.44 eV the *phonon replica/defect band* because its intensity is affected by defects but its structure shows phonon replicas that are superimposed on the defect band. The mid-gap peak has not been extensively studied before in similar materials. Although I have not determined the exact source of this peak, I have analyzed different possibilities that could lead to further understanding in later research.

REFERENCES

1. J. González-Hernández, Elias López-Cruz, D. D. Allred, Worth P. Allred, "Photoluminescence Studies in ZnCdTe Single Crystals," *Journal of Vacuum Science Technology* **A8** (4), 3255 (1990).
2. M. B. Jin, K. M. James, C. E. Jones, and J. L. Merz, "Ion-Implantation Gettering of Impurities in CdTe," (proof).
3. Harold T. Stokes, *Solid State Physics* (Allyn and Bacon, Boston, 1987), pp. 258-60.
4. Jacques I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), pp. 34-36.
5. Harold T. Stokes, *Solid State Physics* (Allyn and Bacon, Boston, 1987), pp. 191-95.
6. Jacques I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), pp. 107-9.
7. Jacques I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), pp. 124-26.
8. Jacques I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), p. 12.
9. Jacques I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), p. 16.
10. Jacques I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), pp. 116-20.
11. Charles Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1971), pp. 372-75.
12. J. S. Blakemore, *Solid State Physics* (Saunders, Philadelphia, 1974), pp. 310-13.

13. Jacques I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), pp. 132-33.
14. Jacques I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), pp. 131-41.
15. Jacques I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), p. 143.
16. Jacques I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), pp. 17-18, 143.
17. Kenneth Zanio, *Cadmium Telluride*, Semiconductors and Semimetals Series, vol. 13 (Academic Press, New York, 1978), p. 138.
18. Kenneth Zanio, *Cadmium Telluride*, Semiconductors and Semimetals Series, vol. 13 (Academic Press, New York, 1978), p. 132-45.
19. D. J. Olego, J. P. Faurie, S. Sivananthan, and P. M. Raccach, "Optoelectronic Properties of CdZnTe Films Grown by Molecular Beam Epitaxy on GaAs Substrates," *Appl. Phys. Lett.* **47** (11), 1173 (1985).
20. C. E. Barnes and K. Zanio, "Photoluminescence in High-resistivity CdTe: In," *J. Appl. Phys.* **46** (9), 3959-64.
21. J. M. Dharmadasa, J. M. Thornton, and R. H. Williams, "Effects of Surface Treatments on Schottky Barrier Formation at Metal/N-type CdTe Contacts," *Appl. Phys. Lett.* **54** (2), 137-39 (1989).
22. F. J. Bryant, and E. Webster, "Threshold Energy for Atomic Displacement in Cadmium Telluride," *Phys. Stat. Sol.* **21**, 315-21 (1967).
23. B. A. Kulp and R. H. Kelley, "Displacement of the Sulfur Atom in CdS by Electron Bombardment," *J. Appl. Phys.* **31** (6), 1057-61 (1960).

BIBLIOGRAPHY

- Ashcroft, Neil W., and N. David Mermin. *Solid State Physics*. San Francisco: Holt, Rinehart and Winston, 1976.
- Barnes, C. E., and Zanio, K. "Photoluminescence in High-Resistivity CdTe: In." *Journal of Applied Physics*. 46 (9): 3959-64.
- Blakemore, J. S. *Solid State Physics*. Philadelphia: W. B. Saunders, 1974.
- Bryant, F. J., and E. Webster. "Threshold Energy for Atomic Displacement in Cadmium Telluride." *Phys. Stat. Sol.* 21, (1967): 315-321.
- Dharmadasa, J. M., J. M. Thornton, and R. H. Williams. "Effects of Surface Treatments on Schottky Barrier Formation at Metal/N-type CdTe Contacts." *Applied Physics Letters*. 54 (2), 9 January 1989: 137-39.
- Feldman, Bernard J., M. L. Wroge, and D. J. Leopold. "CdTe Photoluminescence in HgTe-CdTe Superlattices." *Journal of Applied Physics*. 62 (4), 15 August 1987: 1516-18.
- González-Hernández, J. Elias López-Cruz, D. D. Allred, and Worth P. Allred. "Photoluminescence Studies in $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ Single Crystals." *Journal of Vacuum Science Technology*. A8 (4) (July/August 1990): 3255-59.
- Jin, M. G., K. M. James, C. E. Jones, and J. L. Merz. "Ion-Implantation Gettering of Impurities in CdTe." proof.
- Kittel, Charles. *Introduction to Solid State Physics*. New York: John Wiley & Sons, 1971.
- Kulp, B. A., and R. H. Kelley. "Displacement of the Sulfur Atom in CdS by Electron Bombardment." *Journal of Applied Physics*. 31 (6), June 1960: 1057-61.

- López-Cruz, Elias, J. González-Hernández, D. D. Allred, and W. P. Allred. "Photoconductive Characterization of $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ ($0 < x < .25$) Single Crystal Alloys." *Journal of Vacuum Science Technology*. A8 (3) May/June 1990: 1934-38.
- Mar, H. A., and N. Salansky. "Photoluminescence of CdTe Grown on (001) InSb by Molecular Beam Epitaxy." *Journal of Applied Physics*. 56 (8), 15 October 1984: 2369-71.
- Olego, D. J., J. P. Faurie, S. Sivananthan, and P. M. Raccah. "Optoelectronic Properties of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ Films Grown by Molecular Beam Epitaxy on GaAs Substrates." *Applied Physics Letters* 47 (11) 1 December 1985: 1172-74.
- Pankove, Jacques I. *Optical Processes In Semiconductors*. New York: Dover, 1971.
- Ruckmann, I., M. Petrauskas, V. Netiksis, G. Tamulaitis, and J. Halfpfp. "Investigation of p-CdTe and p- $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ Single Crystals by ps-Laser-Induced Gratings and by Photoluminescence.." *Phys. Stat. Sol. (b)* 142, 629 (1987): 629-40.
- Stokes, Harold T. *Solid State Physics*. Boston: Allyn and Bacon, 1987.
- Willardson, R. K., and Albert C. Beer. *Mercury Cadmium Telluride*. Semiconductors and Semimetals Series, vol. 18. San Diego: Academic Press, 1981.
- Yom, S. S., S. Perkowitz, P. M. Amirtharaj, and J. J. Kennedy. "Picosecond Photoluminescence from Bound Excitons in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$." *Solid State Communications*. 65 (9) 1988: 1055-58.
- Zanio, Kenneth. *Cadmium Telluride*. Semiconductors and Semimetals Series, vol. 13. New York: Academic Press, 1978.

DEEP-LEVEL PHOTOLUMINESCENCE OF $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$

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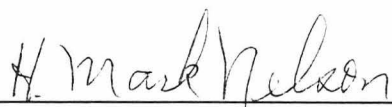
M.S. Degree, December 1991

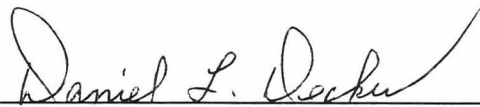
ABSTRACT

$\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ crystals and films were studied by low temperature photoluminescence. The percentage of zinc was varied from zero ($x = 0$) to 10 percent ($x = 0.1$). The spectral region from 0.7 eV to 1.8 eV was investigated. Features in the spectrum that had not been extensively examined before including the phonon replica/defect band and the mid-gap peak were investigated. The phonon replica/defect band is usually centered at 1.44 eV, and its width varies from 150 to 190 meV. In previous studies this peak has been termed the *defect band*. Examination of this peak shows that its intensity is affected by defects but its structure shows phonon replicas superimposed on the defect band. The number of phonon replicas varies. In samples with low zinc content the phonon replica peaks are easy to distinguish, but at higher concentrations they are difficult to discern. The mid-gap peak centered at 1.09 eV has not been extensively studied in these materials. This peak is noted in some samples but not in others. Its intensity relative to other peak intensities increases rapidly with power. The exact source of this peak was not determined, but various possibilities have been analyzed.

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