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Electronic Characterization of Defects in Narrow Gap Semiconductors-Comparison of Electronic Energy Levels and Formation Energies in Mercury Cadmium Telluride, Mercury Zinc Telluride, and Mercury Zinc Selenide

Name of Principal Investigator:

James D. Patterson

James D. Patterson

Period Covered by the Report:

September 19, 1994 to September 19, 1996.

Name and Address of Grantee Institution

Florida Institute of Technology
150 West University Boulevard
Melbourne, FL 32901
(Index Number: 9441)

Grant Number:

GP29-NAG8-1094
George C. Marshall Space Flight Center
Marshall Space Flight Center, AL 35812
(Technical Officers: Sharon Cobb, ES75,
Sandor L. Lehoczky, ES 75)

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Outline

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ABSTRACT

We have used a Green's function technique to calculate the energy levels and formation energy of deep defects in the narrow gap semiconductors mercury cadmium telluride (MCT), mercury zinc telluride (MZT) and mercury zinc selenide (MZS). The formation energy is calculated from the difference between the total energy with an impurity cluster and the total energy for the perfect crystal. Substitutional (including antisite), interstitial (self and foreign), and vacancy deep defects are considered. Relaxation effects are calculated (with molecular dynamics). By use of a pseudopotential, we generalize the ideal vacancy model so as to be able to consider relaxation for vacancies. Different charge states are considered and the charged state energy shift (as computed by a modified Haldane-Anderson model) can be twice that due to relaxation. Different charged states for vacancies were not calculated to have much effect on the formation energy. For all cases we find deep defects in the energy gap only for cation site s-like orbitals or anion site p-like orbitals, and for the substitutional case only the latter are appreciably effected by relaxation. For most cases for MCT, MZT, MZS, we consider x (the concentration of Cd or Zn) in the range appropriate for a band gap of 0.1 eV. For defect energy levels, the absolute accuracy of our results is limited, but the precision is good, and hence chemical trends are accurately predicted. For the same reason, defect formation energies are more accurately predicted than energy level position.

We attempt, in Appendix B to calculate vacancy formation energies using relatively simple chemical bonding ideas due to Harrison. However, these results are only marginally accurate for estimating vacancy binding energies. Since this is a final report, we list in Appendix C, all written reports and publications produced for the grant. We include abstracts and a complete paper that well summarizes our work and which is not yet available.

I. Introduction

Most of our work has been summarized already in previous publications. Thus, what we will do here is to pull this work together with suitable references and include, in the appendices, some parts that are not readily available. We will consider point defects of the following kinds: substitutional (BA where B is the ion that replaces A : if it were an AB alloy, this would be an antisite defect), interstitial (IA), and vacancy (VA).

Deep defects are important because they affect the electrical properties of materials. Carriers in semiconductor materials recombine more readily through deep level states which may act as recombination centers when situated near the center of the energy gap. Deep defects also act as compensators and electron-hole generators. They are characterized by short range, strong potentials originating in the central cell of the defect. Deep defects are localized in real space, while shallow impurities which are often the main supplier of carriers are bound by long range Coulomb potentials, are localized in momentum space, and their energy spectrum is Hydrogen like. An effective mass theory works for shallow levels, but this is seldom the case for deep levels. Deep levels may be in the middle of the gap, or near a band gap edge, or they may even be a resonant level, while low lying shallow levels are Hydrogen like and near a band edge. Because the deep levels are caused by short range potentials, their wave functions are typically fairly compact.

A major thrust of our study is to look at the effects of different charge states on deep defects. The charged state splitting of a deep level in the band gap is the difference between the ionization energy of the neutral impurity and the ionization energy of the impurity in a charged state caused by the addition of electrons or holes. The ionization energy of an impurity in a semiconductor is defined as the energy required to raise an electron (or hole) from an occupied deep level and move it to the conduction (or valence) band. Since the actual charge state of a defect is not in general known, it is important to consider different charge states which will have different energy levels and different formation energies. Also, different charge states may have different barriers for migration and for reacting with other centers. To study charge state splitting, the electron-electron interactions must be included in some approximation. To do this we used the Haldane Anderson model as a simple way to include these interactions. Typical charge state energy shifts of defect levels are about twice that caused by relaxation effects. Because of Coulomb *p. 3*

repulsion for charged states, the negative charged states have higher energy.

There are three important narrow gap semiconductors: MCT, MZT, and MZS of interest to us.^{1,2} The properties of MCT and related compounds are well known, as they are heavily used for making infrared detectors. Their desirable properties include: high optical absorption coefficients, high electron mobilities, low thermal generation rates, moderate cooling temperatures, and tunable band gaps. Their undesirable properties, which must be dealt with include: high Mercury vapor pressure, wide separation of the liquidus and the solidus in the phase diagram, high diffusion coefficients, and softness even though they are brittle. These crystals are hard to grow uniformly under the load of gravity and thus NASA is interested in knowing if they can be grown better in microgravity. Therefore it is necessary to characterize the crystals as grown on the ground as well as in e. g. the Space Shuttle, and it follows that there is an interest in all aspects of the defects of these crystals.

We have predicted the deep defect energy levels and formation energies for charged states of substitutional and interstitial defects, including the effects of relaxation. Although one can see chemical trends in the results for the defect energy levels, absolute location of energy levels depends sensitively on the band structure. Formation energies, involving differences of energies, were predicted with an accuracy similar to that of the chemical trends. All defect sites considered were for tetrahedral symmetry (interstitial sites can be either hexagonal or tetrahedral, but we only considered tetrahedral). For the tetrahedral sites the wave functions are either A_1 (s-like) or T_2 (p-like). In our approximation the diagonal parts of the defect potential are related to the bond length and contain free atom parameters (adjusted for being in the lattice). The off diagonal parts need to be included to treat relaxation which is calculated by molecular dynamics. This off diagonal part of the defect potential contains a constant determined by the host and the impurity. It also contains the host interatomic distance as well as the distance between the impurity and its nearest neighbors (in the relaxed state). Although charged state effect may be greater, relaxation of deep defects is still important because the extension of their wavefunctions mean the position of the level is very sensitive to the effects of nearest and next nearest neighbors. The wave functions of shallow impurities are typically so spread out that relaxation is not an important consideration.

II. Green's Function Calculations

As discussed in more detail in previous papers^{3,4}, we start with the basic tightbinding ideas of Hjalmarson et al.⁵ We add the spin-orbit interaction for II-VI materials following the ideas of Kobayashi et al.⁶ We also adapt the method of Lee et al.⁷ for different charge states and follow Haldane and Anderson⁸ to calculate their effects. The n 's (state occupation numbers in the Haldane Anderson's formalism) are not necessarily integers (in a solid)--they depend on the defect potential and the energy and need to be determined self consistently. Thus the calculation involves an iteration. Except for adapting the work of Li and Myles^{9,10} to include relaxation (which turns out to be essential), the analysis is very similar to the model given in our paper listed in Appendix C(g). Of course, we are also using a virtual crystal approximation to approximately describe the potential for the alloy by an average potential. The use of Green's function techniques to calculate formation energies is new. We only considered anion site p-like and cation site s-like levels. The deep levels for other cases were presumably far from the gap. As far as lowering the potential energy goes, cation sites surrounded by negative ions tend to favor s-like levels (because this keeps negative charges as well separated as possible). Anion sites surrounded by positive ions tend to favor p levels which then the negative charge out to the positive sites. These anion site p levels are also more affected by relaxation than cation site s levels are. Of course, covalent bonding and other effects can complicate the analysis. A major useful property of these materials is the tunability of the band gap with energy. All our calculations were standardized at a band gap of 0.1 eV, corresponding to approximately 12 microns wavelength. This meant an x value of 0.22 for MCT, 0.15 for MZT, and 0.08 for MZS.

III. Deep Levels for Substitutional and Interstitial Defects.

Our results are presented in Figs. 1, 2, and 3. (See the paper included in reference C(g). All figure numbers refer to this paper.) In our notation n stands for nominal. For example if Zn substitutes for Te^{--} , then since Zn in a neutral atomic state has electronic structure ending in $...4s^2$, by $Zn(n)$ we mean Zn with atomic structure $...4s^2 4p^2$, i.e. it is similar to Te^{--} . In Fig. 1 for MCT, we see that the effects of changing charge states can be approximately twice that of relaxation. In Fig. 2 we see that the effects of varying charge states can very easily cause the defect level to move either in or out of the band gap. Comparing Figs. 2a (MZT) and 2b (MZS) we see a similarity in relative value between Zn and Mg defect levels that is, we see the chemical trends are similar in the two materials. Comparing Figs 2 (Substitutional) and 3 (Interstitial), we find that charged state interactions can be higher for interstitials than for substitutional defects. Again comparing Figs 3a and 3b we note the importance of chemical trends. This figure summarizes results for deep levels in interstitial impurities for which we only consider tetrahedral sites. For interstitials, neutral really means neutral they show similar trends as the substitutional case, however charge state splitting seems to be a little larger. Note that charge state splitting can be comparable to the energy gap. For more complete results see reference 4.

IV Formation Energies for Substitutional and Interstitial Defects

We have already discussed the details in a previous paper.⁴ The formation energy is the change in energy necessary to create the defect and can be calculated from:

$$E_F = E_b(\text{crystal with defect cluster}) - E_b(\text{crystal with perfect cluster}).$$

The (negative) binding energies E_b can be calculated from the Green's functions of electrons and from empirical repulsive energies. A typical substitutional defect cluster assumes 17 atoms (one for the substitutional atom, 4 for nearest neighbors, and 12 for next nearest neighbors.) Figs. 4a, 4b, and 4c show some of our results for formation energy--all for MZT--although further work shows that formation energies for the same site and material can be similar. We note that the more electrons we have the higher the energy, presumably due to Coulomb repulsion. The substitutional cation site formation energies tend to be higher than the anion site substitutional energies. We also notice that the cation site interstitials can be significantly different. Figures 4a and 4b present our results for the formation energies of the substitutional cases. The formation energy for the same material on the same site can be quite similar. The formation energy for different charged states can vary widely. The formation energy of negative impurities is larger than positive ones. Cation site formation energies tend to be larger than anion site. The interstitial formation energies tend to be highly variable as shown in Fig. 4c.

V. Vacancies: Deep Levels and Formation Energies

We have introduced a modified vacancy model which allows consideration of lattice relaxation. Our technique, of using a pseudopotential, has already been discussed.⁴ We found very little dependence of formation energy on charge, but relaxation was not negligible. Tables 1 and 2 (again see the paper referenced in appendix C(g)) give our results. Table 1 compares predicted vacancy levels in MCT, MZT, and MZS, while Table 2 compares vacancy formation energies in these three materials. From Table 2 we would predict more vacancies in MZS for the same energy gap, since concentration decreases exponentially with increase in formation energy.

VI. Discussion, Conclusions, and Future Work

The major part of our work is contained in the two Physical Review papers we list in Appendix C. Comparison to experiment for our calculations of defect energy levels is made in the first of these papers. However, there is not much data available to check our formation energy calculations.^{11,12} In fact, we have not been able to find any well identified formation energies that allow unambiguous experimental comparison of our calculations. For complete details of our work, reference can be made to these two Physical Review papers.

Typical of our results are the following:⁴ (a) The charge state energy level shifts of the defects levels were about twice as large as relaxation effects. (b) The more negatively charged the impurity the higher the energy because of Coulomb repulsion. (c) The energy shift of the deep substitutional levels is a rough linear function of the charge state for a particular impurity. (d) Chemical trends in the ordering of the deep levels associated with different impurities for the same charged state are essentially unchanged. (e) Charge state splitting for interstitial impurities tends to be a little larger than for the substitutional ones. (f) Charge state splitting for substitutional impurities may be of order of 0.1 eV and varies only slightly with alloy concentration x . (g) Formation energies for the same material on the same site can be quite similar. (h) The formation energies for different charged states can vary widely. (i) The formation energy for a negative impurity tends to be larger than a positive one. (j) Defect and formation energies for vacancies are predicted not to be heavily dependent on the charged state. (k) Relaxation can appreciably affect the deep levels in vacancies. (l) For native defects, self interstitials had the lowest formation energy while antisites and vacancies had similar formation energies.

Both defect levels (which relate to optical properties) and formation energies (which give an indication of relative concentration) are necessary (but not sufficient) to characterize the defect. In any realistic case, a very strong interaction between theory and experiment is necessary to approach a full characterization. The real situation may involve more complicated centers (and center complexes) than we have considered, so it is not surprising that a full identification of deep defect levels in narrow gap semiconductors is far from being realized.

Future work would involve considering more complicated defects, but it also needs to include (a) a deeper investigation of the role of gravity and convection on nucleating defects, and (b) more understanding of how defect properties can be investigated--particularly by optical means. Although we do not plan to work on it, the affect of magnetic damping on the growth of solid solution semiconductor alloys has become a topic of much current interest.¹ In general, the study of the nature of crystal growth under normal and reduced gravity conditions is still in its infancy.¹

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B. Harrison Chemical Bond Approach

Harrison^{A1-A4}, using bond orbitals has developed some relatively simple equations that estimate bond energies in compound semiconductors. A basic equation that exhibits the bond energy is:

$$E_b = \frac{1}{2}(\epsilon_p^c + \epsilon_p^a) + V_{1a} + V_{1c} - (1 + \alpha_p^2) \sqrt{V_2^2 + V_3^2} - \frac{9}{8}(1 - \alpha_p^2)^2 \frac{(V_{1a})^2 + (V_{1c})^2}{\sqrt{V_2^2 + V_3^2}},$$

where $V_{1a} = (1/4)(\epsilon_p^a - \epsilon_s^a)$ is the anion **metallic energy**, $V_{1c} = (1/4)(\epsilon_p^c - \epsilon_s^c)$ is the cation metallic energy, and these relate to coupling between hybrids on the same atom, $\alpha_c = V_2 / \sqrt{V_2^2 + V_3^2}$ is called the **covalency**, it is complementary to the polarity, $\alpha_p = V_3 / \sqrt{V_2^2 + V_3^2}$ is called the **polarity**, and expresses the probability that an electron is on an anion or a cation, $V_2 = V_2^h$ is called the **covalent energy** for coupling between hybrids on same bond, and $V_3 = V_3^h$ is called the **polar energy** for hybrids, it relates to the difference between hybrid cation and anion energies. Further discussion of these quantities are given in detail by Harrison.

Since we are mainly interested in compound semiconductors with variable concentration x , we use the approximation for any physical quantity Q that

$$Q(\text{Hg}_{1-x}\text{Cd}_x\text{Te}) = xQ(\text{HgTe}) + (1-x)Q(\text{CdTe}).$$

Since each atom has 4 nearest neighbors there are 4 shared bonds broken in forming a vacancy. Thus as an approximation, we assume the vacancy formation energy is

$$E_v = -2E_b.$$

In Table I we calculate V_1 for relevant anions and cations.

Table I

		$-\epsilon_p(A5)$	$-\epsilon_s(A5)$	Computed V_1
anion	Te	9.824 (eV)	19.620 (eV)	2.45 (eV)
cation	Hg	4.872	10.946	1.52
	Cd	4.784	9.611	1.21
	Zn	4.920	10.224	1.33

In Table II, we give needed quantities for compounds.

Table II

	α_p	$\text{Sqrt}(V_2^2+V_3^2)$
HgTe	0.685(A5)	4.2 (eV)
CdTe	0.710 (A5)	4.58
ZnTe	0.544(A1)	5.66

In the following Table, we then give some results and compare to the results of Berding et al.^{A6} We conclude, that these very simple results may give results that are correct in order of magnitude, and may even roughly give trends, but they can hardly be regarded as reliable.

Table III

	E_v	E_v
HgTe	0.7 eV	1.64 (eV) ^{A6}
CdTe	2.32	2.20 ^{A6}
ZnTe	3.68	2.40 ^{A6}
MCT(x=0.22, $E_g=0.1$ eV)	1.06	2.68 ^{Cg}
MZT(x=0.15, $E_g=0.1$ eV)	1.10	3.81 ^{Cg}

C. Publications and Reports Prepared for This Work

- a. Semi-Annual Report--March 19, 1995 (already submitted).
- b. March 1995 BAPS Abstract (included).
- c. November 1995 BAPS Abstract (included).
- d. March 1996 BAPS Abstract (included).
- e. Phys. Rev. **50**, 12903-14910, 1994 (abstract included).
- f. Phys. Rev. **53**, to be published June, 1996(abstract included).
- g. SPIE paper--Aug. 1996 (preprint included).

SEMI-ANNUAL REPORT

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NAME OF POST DOCTORAL RESEARCH ASSOCIATE:

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BULLETIN

OF THE AMERICAN PHYSICAL SOCIETY

16:30

K15 9 Theory of Deep Defects in Narrow Gap Semiconductors. Weigang Li, J.D. Patterson, Florida Institute of Technology ---We use a Green's function technique to calculate the position of deep defects in the narrow gap semiconductors mercury cadmium telluride (MCT), mercury zinc telluride (MZT) and mercury zinc selenide (MZS). Substitutional (including antisite), and interstitial (self and foreign) deep defects are considered. Relaxation effects are included and they can be greater for the interstitial case than the substitutional one. For all cases we find deep defects in the energy gap only for cation site s-like orbitals or anion site p-like orbitals, and for the substitutional case only the latter are appreciably effected by relaxation. For substitutional impurities in MCT, MZT, MZS, we consider x (the concentration of Cd or Zn) in the range $0.1 < x < 0.3$ and also for both substitutional and interstitial cases we do extensive calculations for x values appropriate to a band gap of 0.1 eV. For the substitutional case we find that I, Se, S, Rn, and N are possible defect candidates to form cation site, s-like levels in MCT and Zn and Mg are for anion site, p-like levels. Similarly in MCT for the interstitial case we find deep defect levels in the band gap for Au, Ag, Hg, Cd, Cu, and Zn for the cation site, and N, Ar, O, and F for the anion site. For the substitutional cases we have some examples where relaxation moves the levels into the band gap, whereas for interstitial cases we have examples where relaxation moves them out of the band gap. We find that the chemical trends of defect levels in MZT is similar to that in MCT, however, the same conclusion doesn't hold for MZS. The absolute accuracy of our results is limited, but the precision is good, and hence chemical trends are accurately predicted. Supported by NASA Grant NAG8-941.

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ED 16 Formation Energies for Substitutional Impurities and Interstitials in Mercury Cadmium Telluride, Mercury Zinc Telluride and Mercury Zinc Selenide. J.D. PATTERSON AND WEIGANG LI, Department of Physics and Space Sciences, Florida Institute of Technology, Melbourne, FL 32901. We use Green's function techniques to calculate the formation energies. The formation energy is calculated from the difference between the total energy with an impurity cluster and the total energy for the perfect crystal. A cluster from an infinite crystal is used and thus the periodicity of the host crystal is accounted for. The total energy of the cluster is a sum of one electron energies and the repulsion energy. It contains a correction for double counting in summing the one electron energies. Relaxation of neighbors and different charge states are considered. Results will be given for several examples including both anion and cation site impurities. Supported by NASA Grant NAG8-1094.

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10:00

Q26 11 Energy Levels and Formation Energies of Deep Defects in Narrow Gap Semiconductors J. D. PATTERSON, WEIGANG LI, *Florida Institute of Technology* — We use a Green's function technique and consider the semiconductors mercury cadmium telluride (MCT), mercury zinc telluride (MZT) and mercury zinc selenide (MZS). The formation energy is calculated from the difference between the total energy with an impurity cluster and the total energy for the perfect crystal. Substitutional (including antisite), interstitial (self and foreign), and vacancy deep defects are considered. Relaxation effects are calculated (with molecular dynamics) and their energy shift can be greater for the interstitial case than the substitutional one. The charged state energy shift (as computed by a modified Haldane-Anderson model) can be twice that of relaxation. By use of a pseudopotential, we generalize the ideal vacancy model so as to be able to consider relaxation. Calculations for different charged states for the vacancies showed little effect on the formation energy. Chemical trends are accurately predicted and defect formation energies are more accurately estimated than the absolute energy level position. Supported by NASA Grant NAG8-1094.

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Deep defects in narrow-gap semiconductors

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We use a Green's-function technique to calculate the position of deep defects in narrow-gap semiconductors. In order to predict chemical trends, we examine the effects of several different chemical elements. Substitutional (including antisite), (ideal) vacancy, and interstitial (self and foreign) deep defects are considered. The compounds considered are mercury cadmium telluride (MCT), mercury zinc telluride (MZT), and mercury zinc selenide (MZS). The effect of relaxation of neighbors is considered for the substitutional and interstitial cases. Relaxation effects can be greater for the interstitial case than for the substitutional one. For all cases we find deep defects in the energy gap only for cation-site *s*-like orbitals or anion-site *p*-like orbitals, and for the substitutional case only the latter are appreciably affected by relaxation. For substitutional impurities in MCT, MZT, and MZS, we consider x (the concentration of Cd or Zn) in the range $0.1 < x < 0.3$ and also for both the substitutional and interstitial cases we do extensive calculations for x values appropriate to a band gap of 0.1 eV. Specific results are given in figures and tables and comparison to experiment and other calculations is made in a limited number of cases. For the substitutional case we find that I, Se, S, Rn, and N are possible defect candidates to form cation-site, *s*-like levels in MCT, and Zn and Mg are for anion-site, *p*-like levels. Similarly, in MCT for the interstitial case we find deep defect levels in the band gap for Au, Ag, Hg, Cd, Cu, and Zn for the cation site, and N, Ar, O, and F for the anion site. For the substitutional cases we have some examples where relaxation moves the levels into the band gap, whereas for interstitial cases we have examples where relaxation moves them out of the band gap. We find that the chemical trends of defect levels in MZT are similar to that in MCT. However, the same conclusion does not hold for MZS. We have also used perturbation theory (see the Appendix) to look at the effect of nonparabolicity on shallow donor levels, and find it can increase the binding by 10% or so. Although the absolute accuracy of our results is limited, the precision is good, and hence chemical trends are accurately predicted. Further work involves calculating the effect of charged-state interactions and the effect of relaxation on vacancy levels.

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ELECTRONIC AND FORMATION ENERGIES FOR DEEP DEFECTS IN NARROW GAP SEMICONDUCTORS

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ABSTRACT

We consider the charged states of certain deep defects in the narrow gap semiconductors mercury cadmium telluride, mercury zinc telluride, and mercury zinc selenide. We predict the values of the deep defect energy levels and also the formation energy of the defects. For each charged state we include the effect of relaxation. We consider substitutional and interstitial anions and cations as well as vacancies. We use Green's function techniques throughout and adapt the Haldane-Anderson model to consider the effects of different charged states. By use of a pseudopotential we generalize the ideal vacancy model so as to be able to consider relaxation. As always, chemical trends were predicted with considerably more accuracy than the absolute location of the energy levels. Formation energies, involving differences, were predicted with an accuracy similar to that of chemical trends. The more negatively charged the impurity, the higher the energy except that the vacancy energy did not depend strongly on the charge. Typical charge state energy shifts of defect levels are about twice that caused by relaxation effects. Formation energies for defects in the same material and at the same site were quite similar while the formation energy for different charged states could vary considerably. If one considered only native defects, self interstitials had the lowest formation energy while for antisites and vacancies the results were similar.

Formation energies and energy levels of deep defects in narrow gap
semiconductors

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ABSTRACT

We use a Green's function technique for deep defect energy level calculations in mercury cadmium telluride (MCT), mercury zinc telluride (MZT), and mercury zinc selenide (MZS). The formation energy is calculated from the difference between the total binding energy with an impurity cluster and with a perfect cluster. These alloys are among those that have been experimentally grown in microgravity aboard the Space Shuttle. To evaluate the quality of these crystals, it is necessary to characterize them, and one important aspect of this characterization is the study of deep defects which can limit carrier lifetime. Relaxation effects are calculated with molecular dynamics. The resulting energy shift can be greater for the interstitial case than the substitutional one. Relaxation in vacancies is also considered. The charged state energy shift (as computed by a modified Haldane-Anderson model) can be twice that caused by relaxation. However, different charged states for vacancies had little effect on the formation energy. For all cases we considered the concentration of Cd or Zn in the range appropriate for a band gap of 0.1 eV. The emphasis of our calculation is on chemical trends. Only limited comparison to experiment and other calculations is possible, but what there is supports the statement that our results are at least of the right order of magnitude.

Keywords: narrow gap semiconductors, formation energies, deep defects, Mercury Cadmium Telluride, Mercury Zinc Telluride, Mercury Zinc Selenide

1. INTRODUCTION

Because of gravity induced convective flows, homogeneous II-VI semiconducting alloys seem to be inherently difficult to grow in bulk and therefore a microgravity growth environment has been considered.¹ The crystal growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ (MCT), $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$ (MZT), and $\text{Hg}_{1-x}\text{Zn}_x\text{Se}$ (MZS) both on earth and in microgravity has been investigated by Lehoczy² and others. The x values of particular interest were for energy gaps appropriate for infrared sensing (E_g of order 0.1eV). Significant topological differences were shown by surface photomicrographs of space- and ground-grown samples for a $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$ crystal. Bulk $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ has also been grown successfully in microgravity on the Space Shuttle. Although defects are well known to be of extreme importance in semiconductors, both for introducing desirable and undesirable properties, the effect of crystal growth on their nucleation is not well understood particularly as it relates to the effect of fluid flows on ground and space grown crystals. Microgravity should allow this problem to be studied as it may well reduce fluid flows. There are also complications in space grown crystals due to Maragoni convection and g-jitter.

To evaluate the quality of the crystals grown in space and on the ground, it is necessary to characterize them, and one important aspect of this characterization is the study of deep defects which can limit carrier lifetime. Characterization includes the specification of defects as to number and type. Experimental identification from photoluminescence or deep level transient spectroscopy can greatly benefit from theoretical guidance indicating which defects cause which energy levels. The calculation of formation energies is also useful as this relates to the expected concentration of different defects.

We use a Green's function technique for calculations in mercury cadmium telluride, mercury zinc telluride, and mercury zinc selenide. The formation energy is calculated from the difference between the total binding energy with an impurity cluster and the total binding energy with a perfect cluster. Relaxation effects are calculated (with molecular dynamics). By use of a pseudopotential, we have generalized the ideal vacancy model so as to be able to consider relaxation. Since the actual charge state of a defect is not in general known, it is important to consider different charge states which will have different energy levels and different formation energies. Also, different charge states may have different barriers for migration and for reacting with other centers. The charged state energy shift is computed by a modified Haldane-Anderson model. For all cases we considered the concentration of Cd or Zn in the range appropriate for a band gap of 0.1 eV which corresponds to an threshold absorption wavelength of about 12 microns or within the 8 to 12 micron absorption window. For MCT this means $x=0.22$, MZT(0.15) and MZS(0.08).

In section 2 we briefly discuss our calculational method using Green's functions. In section 3 we give example results for substitutional and interstitial defects. In section 4 we briefly discuss our methods for calculating formation energy for deep defects and give some results. In section 5, results for formation and deep levels for vacancies are given and our quantitative results with qualitative conclusions are summarized in section 6. Finally in the appendix we sketch out the essential ideas by discussing a one dimensional model.

2. GREEN'S FUNCTION CALCULATION

As discussed in more detail in previous papers^{3,4}, we start with the basic ideas of Hjalmarson et al.⁵ We add the spin-orbit interaction for II-VI materials following the ideas of Kobayashi et al.⁶ We also adapt the method of Lee et al.⁷ for different charge states and follow Haldane and Anderson⁸ to calculate their effects. Except for adapting the work of Li and Myles^{9,10} to include relaxation, the analysis is very similar to the model given in the appendix.

3. RESULTS FOR SUBSTITUTIONAL AND INTERSTITIAL DEFECTS

Our results are presented in Figs. 1, 2, and 3. In our notation "n" stands for nominal. For example if Zn substitutes for Te^{-} , then since Zn in a neutral atomic state has electronic structure ending in $...4s^2$, by Zn(n) we mean Zn with atomic structure $...4s^24p^2$, i.e. it is similar to Te^{-} . In Fig. 1 for MCT, we see that the effects of changing charge states can be approximately twice that of relaxation. In Fig. 2 we see that the effects of varying charge states can very easily cause the defect level to move either in or out of the band gap. Comparing Figs. 2a (MZT) and 2b (MZS) we see a similarity in relative value between Zn and Mg defect levels that is, we see the chemical trends are similar in the two materials. Comparing Figs 2 (substitutional) and 3 (interstitial), we find that charged state interactions can be higher for interstitials than for substitutional defects. Again comparing Figs 3a and 3b we note the importance of chemical trends.

4. FORMATION ENERGIES FOR SUBSTITUTIONAL AND INTERSTITIAL DEFECTS

We have already discussed the details in a previous paper.⁴ The formation energy is the change in energy necessary to create the defect and can be calculated from: $E_F = E_b(\text{crystal with defect cluster}) - E_b(\text{crystal with perfect cluster})$. The (negative) binding energies E_b can be calculated from the Green's functions of electrons and from empirical repulsive energies. A typical substitutional defect cluster assumes 17 atoms (one for the substitutional atom, 4 for nearest neighbors, and 12 for next nearest neighbors.) Figs. 4a, 4b, and 4c show some of our results for formation energy--all for MZT--although

further work shows that formation energies for the same site and material can be similar. We note that the more electrons we have the higher the energy, presumably due to Coulomb repulsion. The substitutional cation site formation energies tend to be higher than the anion site substitutional energies. We also notice that the cation site interstitials can be significantly different.

5. VACANCIES: DEEP LEVELS AND FORMATION ENERGIES

We introduce a modified vacancy model which allows consideration of lattice relaxation. Our technique, of using a pseudopotential, has already been discussed.⁴ We found very little dependence of formation energy on charge, but relaxation was not negligible. Tables 1 and 2 give our results. Table 1 compares predicted vacancy levels in MCT, MZT, and MZS, while Table 2 compares vacancy formation energies in these three materials. From Table 2 we would predict more vacancies in MZS for the same energy gap.

Table 1	
Deep levels of Vacancies in MCT, MZT, and MZS	
(Measured from maximum valence band edge)	
Alloy	Energy (eV)
MCT	-0.18
MZT	-0.25
MZS	0.06

Table 2	
Formation Energies of Vacancies MCT, MZT, and MZS	
Alloy	Energy (eV)
MCT	2.68
MZT	3.81
MZS	1.75

6. SUMMARY

Of course the first thing one would like to do after making a sequence of calculations is to compare them with experiment and other calculations. Unfortunately, there isn't much information available for making direct comparison. We mention two examples which at least indicate that we have results which are the right order of magnitude. For a possible cation site deep energy level formed by interstitial mercury in MCT, experiment gives $0.7E_g$ ¹¹ and our calculation gives $0.83 E_g$. For antisite Te on a Hg site in MCT Sher¹² calculates a formation energy of 4.53 eV, and we find 3.7 eV. Future work could involve checking our method by doing calculations on materials where very accurate density functional techniques have been applied.

Our results can be qualitatively summarized as follows: (a) Charge state energy shifts can be double those due to relaxation; (b) The more negatively charged the impurity, the higher the energy because of Coulomb repulsion; (c) Chemical trends in the ordering of deep levels associated with different impurities for the same charged state are essentially unchanged. For example, $Zn(n) > Mg(n)$ in MCT and the same is true for MZT and MZS. In other words we believe our precision is greater than our accuracy; (d) Charged state splitting for interstitial impurities tends to be a little larger than for substitutional ones;

(e) Formation energies involving the same site and material can be quite similar. For example in MCT:Zn(n) has formation energy 2.8 eV, Mg(n): 2.7 eV, and Cd(n): 2.85 eV.

7. ACKNOWLEDGMENTS

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8. APPENDIX: THE HALDANE AND ANDERSON MODEL IN ONE DIMENSION

8.1. Substitutional impurity

The model we discuss here is a one dimensional tight binding model. We give a brief summary of the model in order to show how Green's function calculations can be used to calculate defect levels and in particular to exhibit the generalization of the model with the ideas of Haldane and Anderson in order to calculate the effects of charged states.

Following Economu¹³, the one dimensional crystal has Hamiltonian:

$$H_0 = \sum_m |m\rangle e_0 \langle m| + V \sum'_{nm} |n\rangle \langle m|. \quad (1a)$$

The sum is restricted to nearest neighbors and the prime means n not equal to m, e_0 is an "atomic energy," and V characterizes the strength of the hopping between sites. The substitutional impurity in the lattice at site q is represented by

$$H_1 = |q\rangle e \langle q|, \quad (1b)$$

where e is the change in "strength" of the binding at q due to the impurity. The unperturbed Hamiltonian H_0 can be diagonalized by going to the Bloch representation $|k\rangle$. We find that the band of energies is given by

$$E_k = e_0 + 2V \cos(ka). \quad (2a)$$

8.2. Green's functions

Green's functions can be used to predict the energy levels when the perturbation due to the substitutional defect is included. They are defined for Hamiltonian H by

$$G(z) = (z - H)^{-1}. \quad (3)$$

Calling G_0 the Green's function due to H_0 , it is straightforward to show the discrete eigenvalues E_p due to the Hamiltonian $H_0 + H_1$ are given by

$$G_0(q, q, E_p) = 1/e, \quad (4)$$

where $G_0(q, q) = \langle q | G_0 | q \rangle$. It is also relatively easy to show that the diagonal element of the unperturbed Green's function is:

$$G_0(q,q,E_p)=[(E_p-e_0)^2-4V^2]^{-1/2}. \quad (5)$$

In summary, the unperturbed Green's function (5) can be calculated once the band structure is known. Localized functions are used in the construction of the perturbed Hamiltonian from which a relationship can be derived between G_0 and the perturbation (4). The defect energy E_p can then be calculated using (4) and (5).

In three dimensions, similar results are obtained. A tight binding Hamiltonian can be constructed by a fit to the actual band structure calculations and from this the Green's function for the perfect Crystal is determined. This, combined with the specification of the defect potential determines the energy levels of the defect. The primary advantage of a Green's function calculation is that it treats an isolated defect in an otherwise perfect crystal with the same accuracy that one chooses to treat the corresponding perfect crystal.

8.3. Haldane and Anderson approach for charge states

Each defect can exist in different charge states. The actual charge state of the defect may be unknown. The location of the energy level (in or out of the gap) is highly dependent on the charge state, particularly for narrow gap semiconductors. We now use a one dimensional model to treat, in the Haldane Anderson approximation, different charge states with different Coulomb interactions.

Combining Eqs. (4) and (5) we find for the defect energy level below the band that

$$E_p=e_0-[e^2+4V^2]^{1/2}. \quad (6)$$

In order to allow for different charge states, we double the number of states by allowing each state to have a spin degeneracy corresponding to the up and down spins, ($\sigma= +1/2, -1/2$). The perturbing Hamiltonian representing the substitutional impurity is now generalized to have a sum over σ . Following the usual assumptions of Hjalmarson, we determine e by

$$e=\beta(E_{imp}-E_{host}), \quad (7)$$

where E_{host} is the host atomic orbital energy e_0 , and E_{imp} is the orbital energy of the atom which forms a defect in the substitutional case. E_{host} and β are fixed empirical parameters and by the theory of Haldane and Anderson we assume:

$$E_{imp}=a + bn_q, \quad (8)$$

where due to degeneracy n_q is the same for either spin and a and b are empirical constants. The use of the Feynman-Hellman theorem allows one to relate n_q to dE/de . Combining this with (7) and (8) we find:

$$e=\beta(c_1 + c_2 dE_p/de), \quad (9)$$

where $c_1=a-e_0$ and c_2 is also known but different for the one and two electron case. Eqs. (6) and (9) can

then be solved self consistently for the defect energy. In one dimension we can carry this out analytically, but in three dimensions the self consistency is achieved numerically. In one dimension, the charge state splitting is easily evaluated by looking at the difference of ionization energy in the one and two electron cases. In Fig. 5 we see that the charged state interaction increases as the strength of the defect increases.

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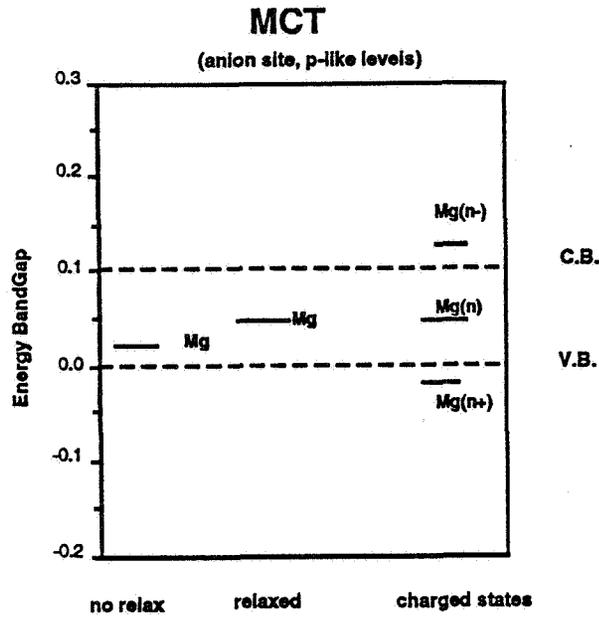


Figure 1: Deep levels for a substitutional impurity in MCT showing effects of relaxation and charged states (with relaxation).

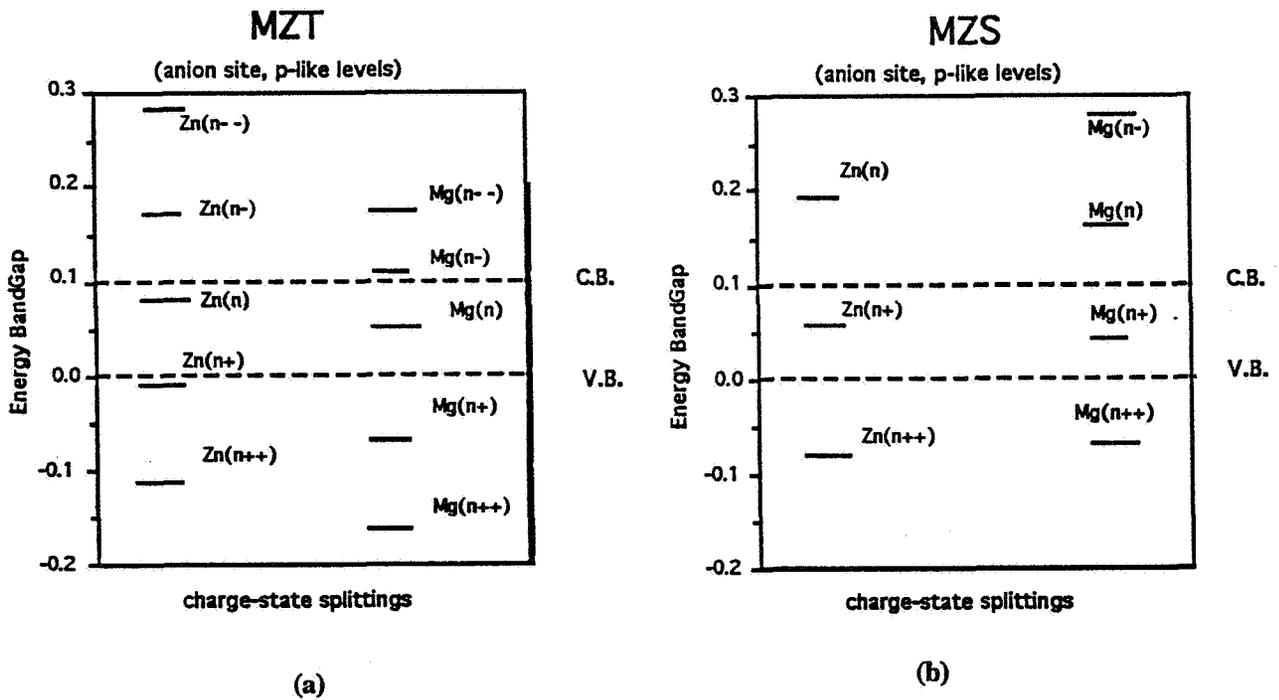


Figure 2: Deep levels for charged states of substitutional anion site defects. (a) MZT, (b) MZS.

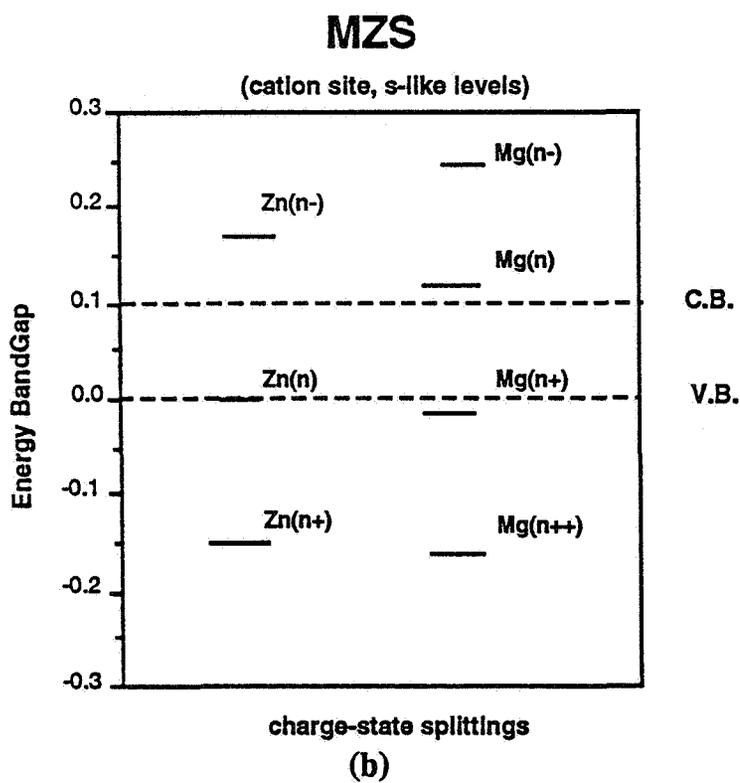
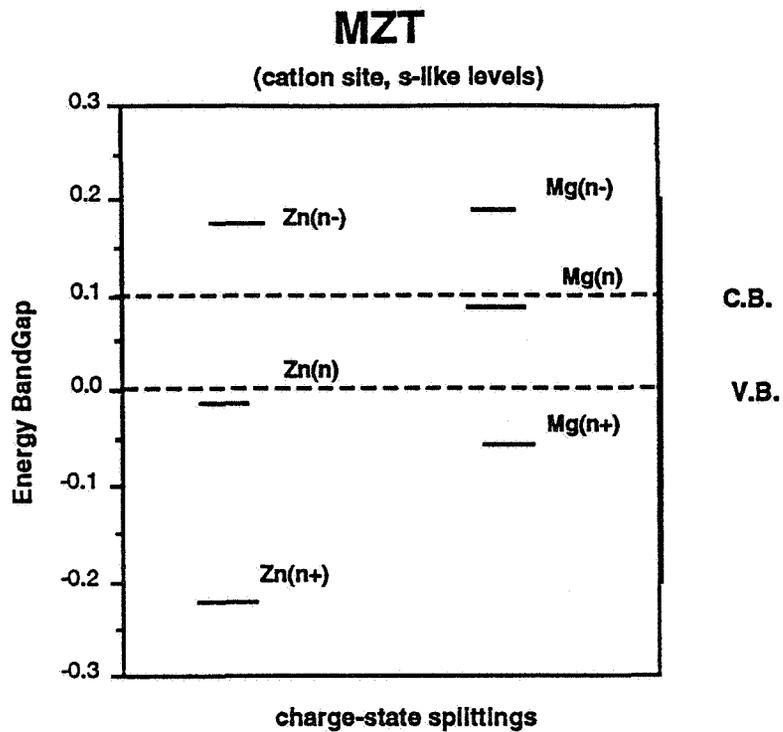
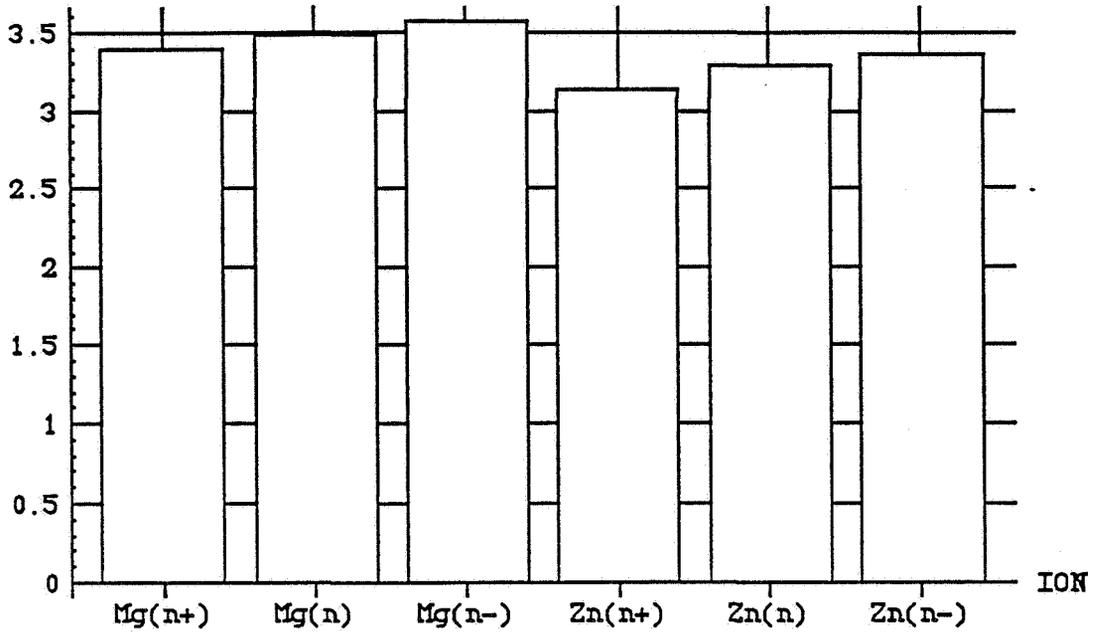


Figure 3: Deep levels for charged states of interstitial impurities. (a) MZT, (b) MZS.

FORMATION ENERGY (eV)

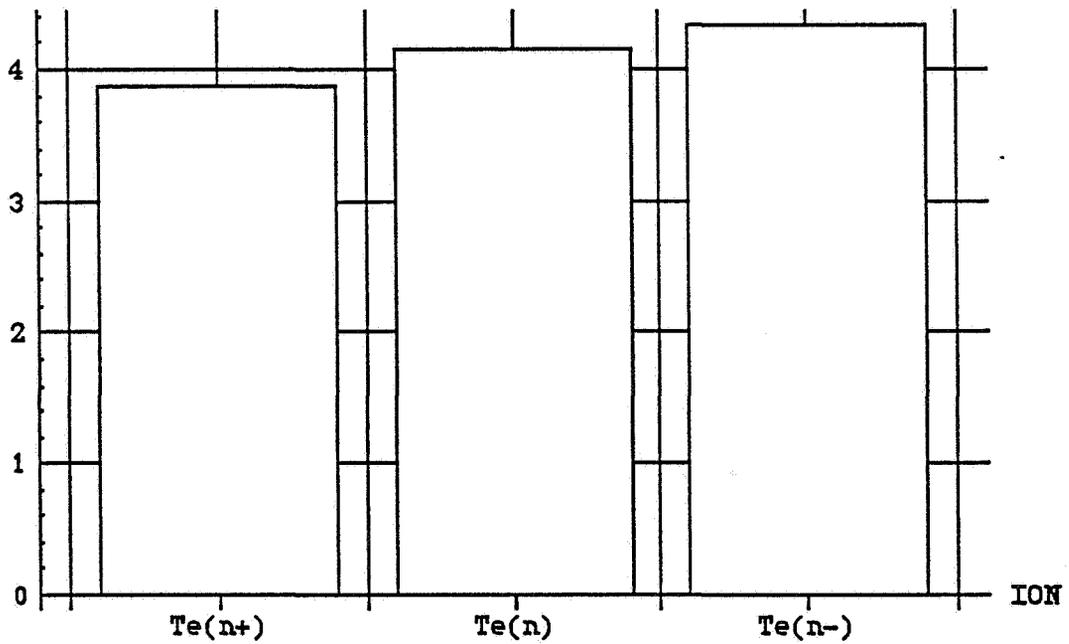
MZT ANION SITE, SUBSTITUTIONAL



(a)

FORMATION ENERGY (eV)

MZT CATION SITE, SUBSTITUTIONAL

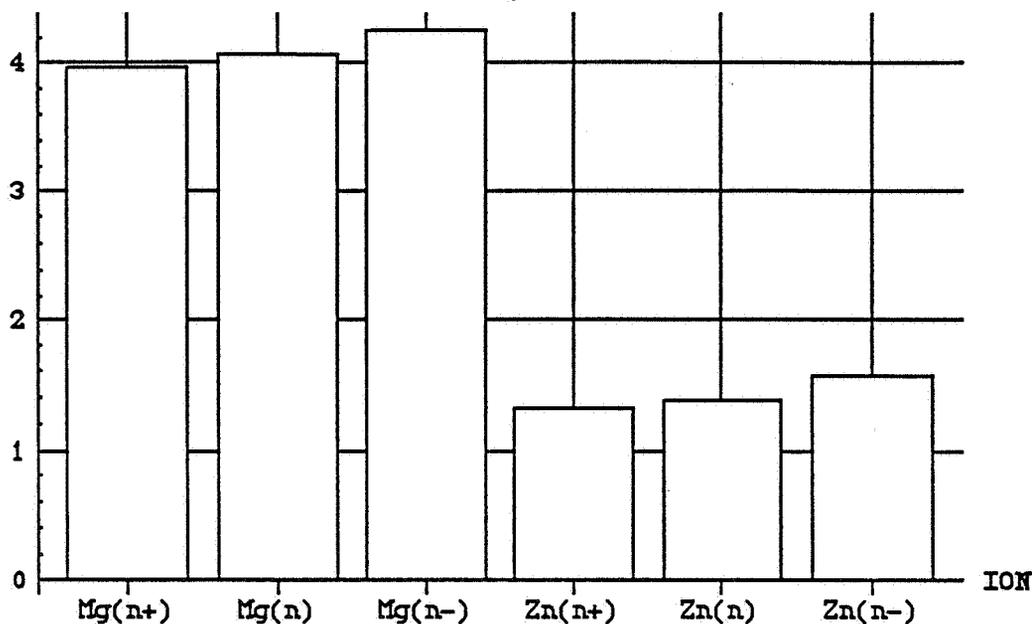


(b)

Figure 4: Formation energies for different charged states. (a) MZT anion substitutional (b) MZT cation substitutional.

FORMATION ENERGY(eV)

MZT CATION SITE, INTERSTITIAL



(c)

Figure 4 (continued): Formation energies for different charged states.
(c)MZT cation interstitial.

CHARGE STATE SPLITTING IN ONE DIMENSION

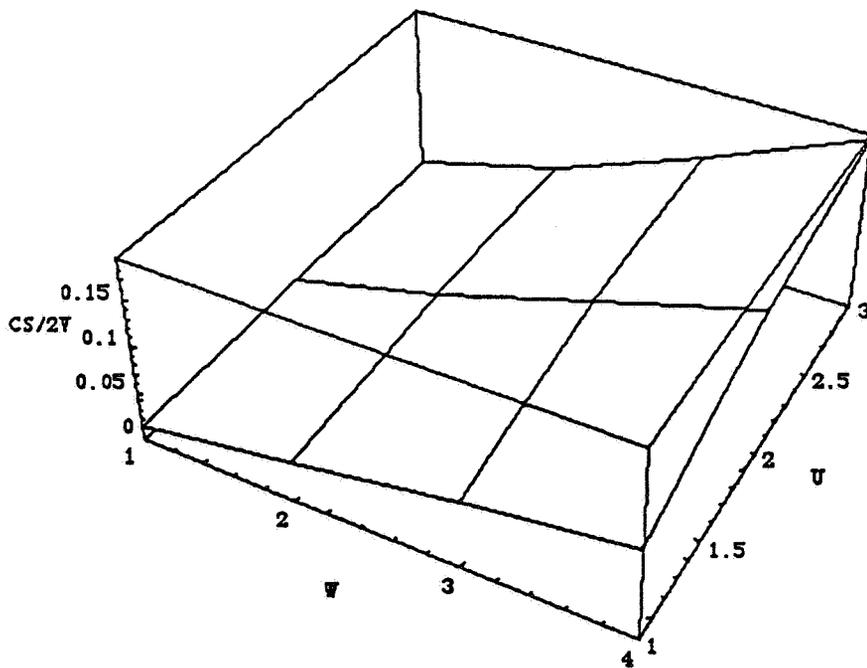


Fig. 5: Charge State (CS) Splitting in One Dimension, $W=(4/3) \beta(a-e_0)$, $U=(5/3) \beta b/V$.