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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 $Hg_{1-x}Cd_xTe$ (MCT), $Hg_{1-x}Zn_xTe$ (MZT), and $Hg_{1-x}Zn_xSe$ (MZS) both on earth and in microgravity has been investigated by Lehoczky[2] 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 $Hg_{1-x}Zn_xTe$ crystal. Bulk $Hg_{1-x}Cd_xTe$ 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.

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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 dimentional model.

2. GREEN'S FUNCTION CALCULATION

As discussed in more detail in previous papers[3,4], we start with the basic ideas of Hjalamarson 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 Anderson[8] 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 ...$4s^2 4p^2$, 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.

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: $E_F=E_b$(crystal with defect cluster)-E_b(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 subsitutional 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

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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 that 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 indicates 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 Sher[12] 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;

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(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 Economu[13], the one dimensional crystal has Hamiltonian:

$$Ho= \Sigma_m |m\rangle e_0 \langle m| + V\, \Sigma'_{nm} |n\rangle\langle m|. \tag{1a}$$

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

$$H_1 = |q\rangle e \langle q|, \tag{1b}$$

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

$$E_k = e_0 + 2V\mathrm{Cos}(ka). \tag{2a}$$

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

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

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

$$G_0(q,q,E_p)=1/e, \tag{4}$$

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:

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

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_o 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

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

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

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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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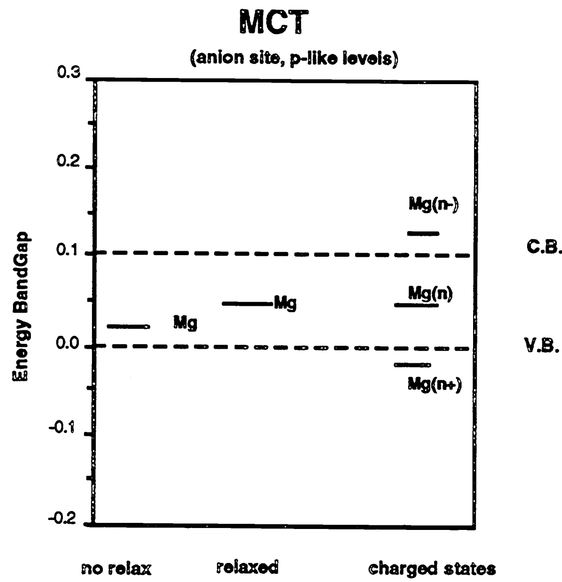

Figure 1: Deep levels for a substitutional impurity in MCT showing effects of relaxation and charged states (with relaxation).

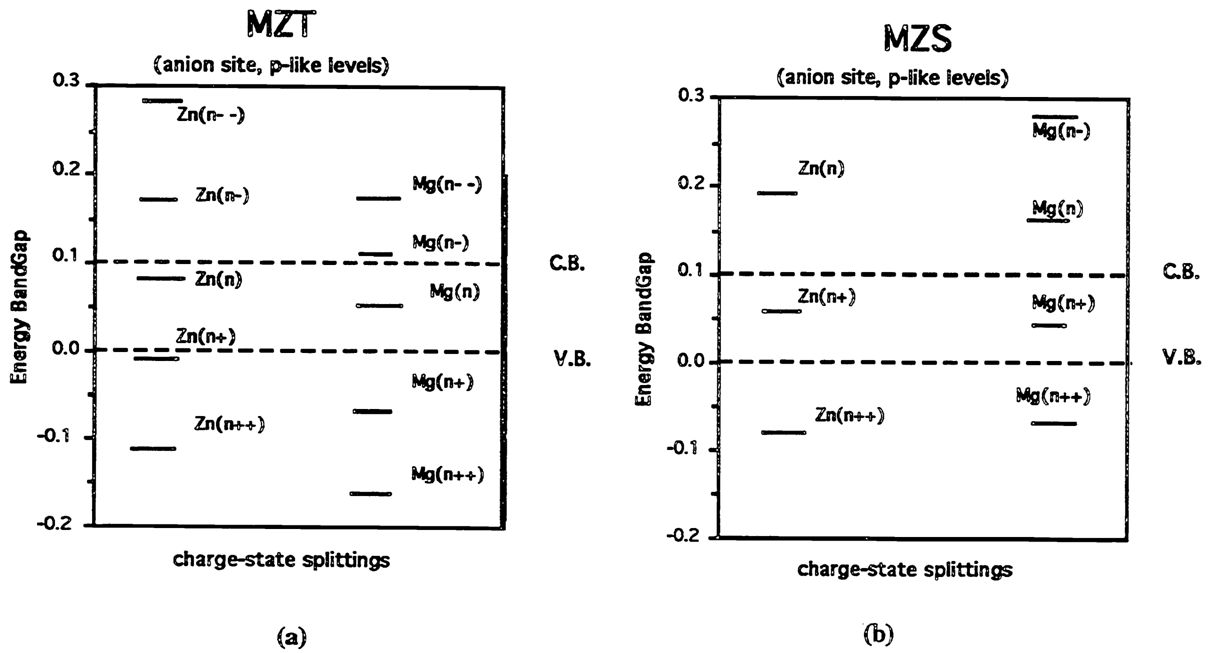

Figure 2: Deep levels for charged states of substituional anion site defects.
(a) MZT, (b) MZS.

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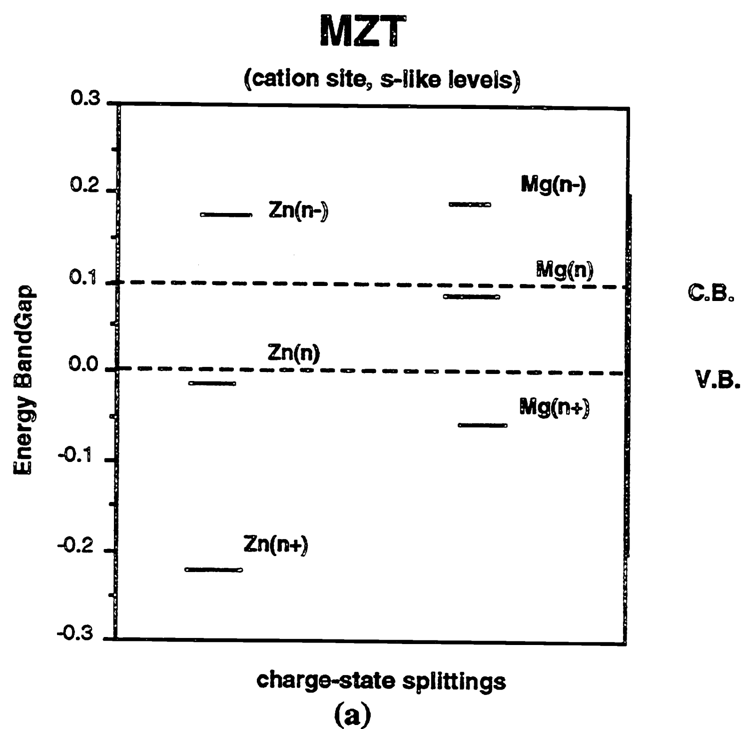
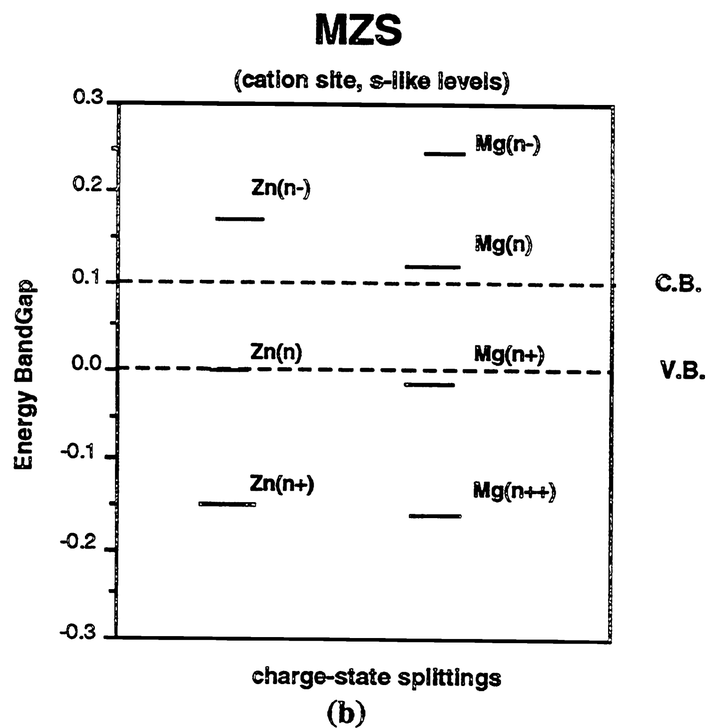


(a)



(b)

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

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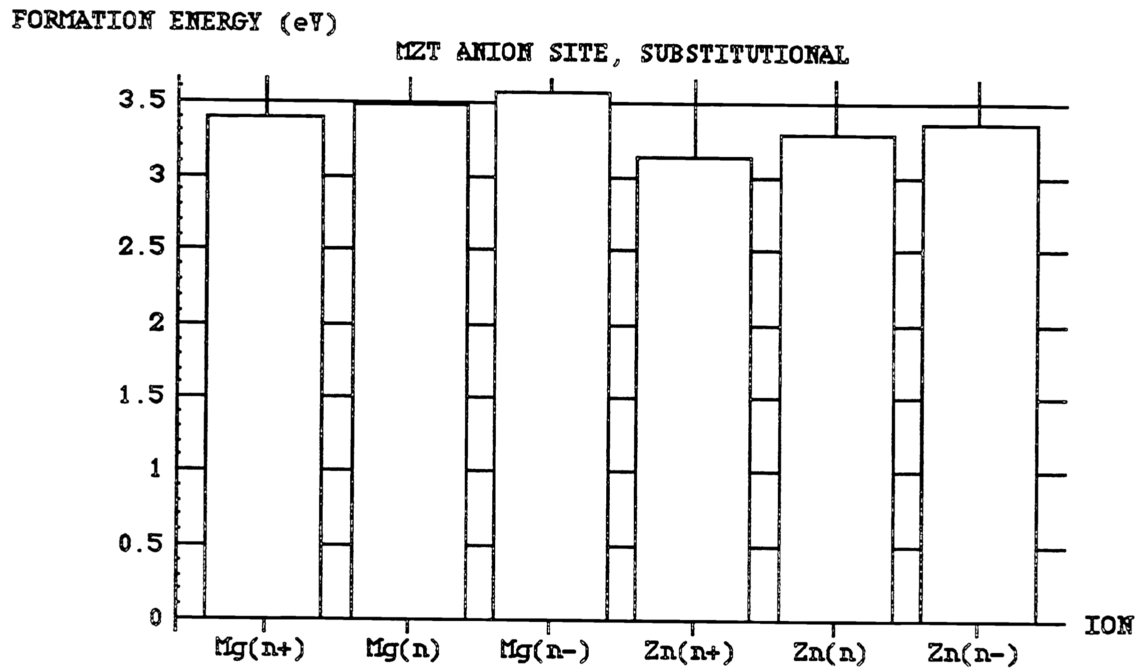
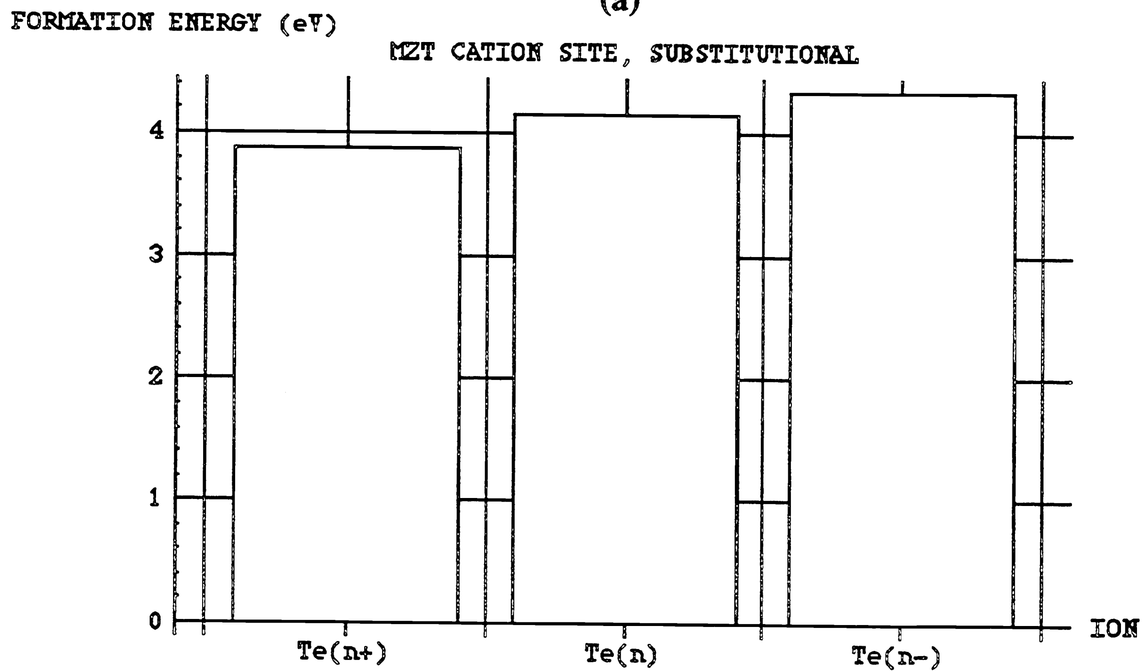


(a)



(b)

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

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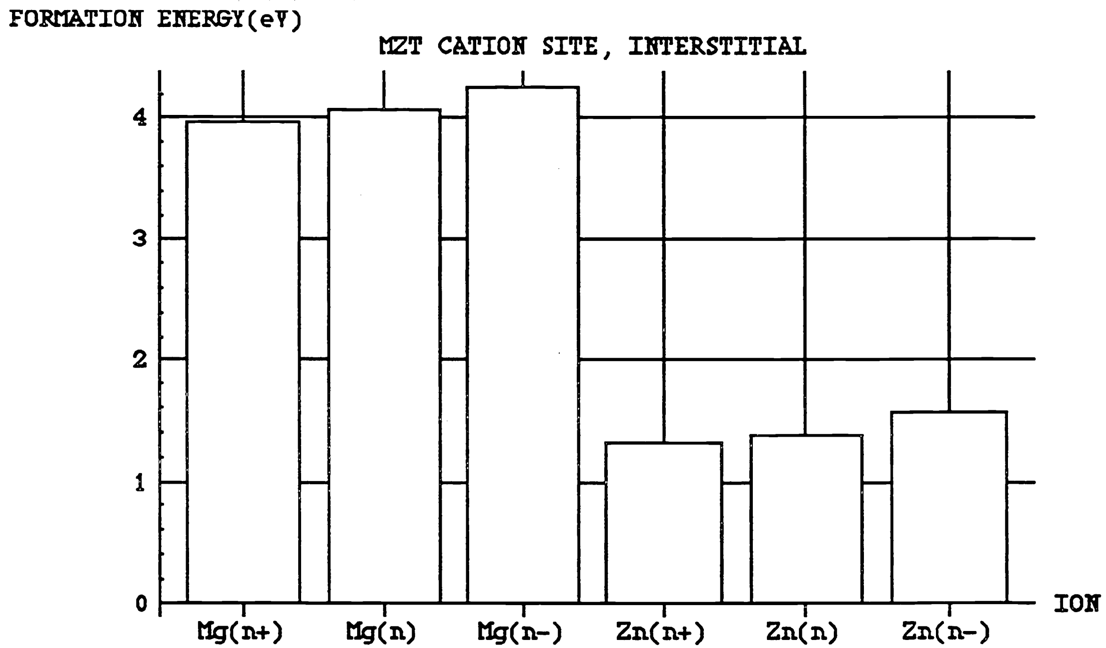

(c)

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

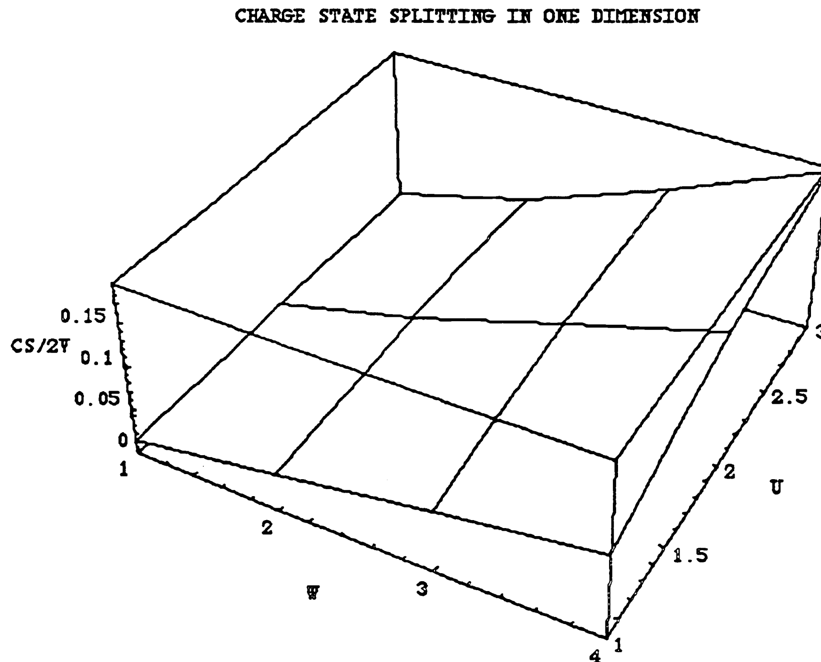

Fig. 5: Charge State (CS) Splitting in One Dimension, $W=(4/3)\beta(a-e_0)$, $U=(5/3)\beta b/V$.

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