



# Lattice Distortion in $Zn_{1-x}M_xO$ (M=V,Mn) and Vegard's Law

## KEYWORDS

Lattice distortion, tight binding, Hybrid energy, overlap parameter

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**ABSTRACT** In this paper the variation in bond length in vanadium and manganese doped zinc oxide (for  $x=0$  to 0.5) has been computed using modified tight binding approach. Modifications in hybrid energy and overlap parameter have been introduced in the Harrison's method which resulted into increase in accuracy and decrease in the number of iterations in the calculation of bond length. Results indicate that the composition dependence of bond length in  $Zn_{1-x}M_xO$  is non-linear and deviates from Vegard's law. Mismatch of ionic size and volume deformation play the major role for the non-linear composition dependence of bond length.

## 1. INTRODUCTION

Increasing interest has been shown in recent years in the study of zinc oxide (ZnO) due to the industrial demand for optoelectronic devices operating in the deep blue or ultraviolet region (Paul Joseph and Venkateswaran(2011);Maensiri et al (2007);Schleife et al(2006)). Zinc oxide (ZnO), a direct wide band gap semiconductor, crystallizes in Wurtzite phase under natural conditions with  $a=3.25\text{\AA}$  and  $c=5.12\text{\AA}$ . It has many attractive properties such as large energy gap (3.37eV), large exciton binding energy (60 meV at room temperature), good piezoelectric characteristic, chemical stability and biocompatibility. ZnO alloyed with "3d" transition metal ions has recently been identified as a promising material for its application in the field of SPINTRONICS (Labidi et al(2010)). Recently, validity of Vegard's law (Vegard (1921)) has been reported in ZnO alloyed with Be and Mg (Duan et al(2008);Amrani et al(2007)). On the other hand Fan et al has reported for deviation from Vegard's law in  $Mg_xZn_{1-x}O$  and  $Ca_xZn_{1-x}O$  (Fan et al(2008)). Similar results have also been reported in some II-VI and III-V ternary alloys (Liou et al (2005);Branicio et al (2003);Carrier et al (2005);Labidi et al (2009);Sajid et al (2012)).

In  $Mg_xZn_{1-x}O$ , lattice parameter and lattice energy have been reported to follow Vegard's law, but the bulk modulus and band gap have been reported to exhibit departure from it (Amrani et al (2007)). Because of these conflicting reports concerning validity of Vegard's law in semiconductor alloys, it was thought worth to find the degree of obedience of Vegard's law in transition metal doped systems  $Zn_{1-x}M_xO$  (M=V,Mn) in the study of bond length.

## 2. THEORETICAL APPROACH:

In this study Harrison's Universal parameter tight binding (UPTB) approach has been utilized in the estimation of bond-length in  $Zn_{1-x}M_xO$  systems. Details of the theoretical approach has been described elsewhere( Harrison (1980)). This is an elegant and simple method to compute bond-length. However, two modifications have been suggested, in this study, in the Harrison's approach – one in the calculation of hybrid energy and the other in the estimation of the overlap parameter. This modification has led to improve the degree of accuracy of results. In the estimation of hybrid energy, the d-shell energy of transition metals have been incorporated in appropriate proportion in the doped systems. The weighted average of the overlap parameters of concerned elements involved in the semiconductor alloys has been used instead of geometric mean. In this modification, the overlap parameter is calculated as where the weightage corresponding to the respective periods of Zn and O have been incorporated.

## 3. RESULTS AND DISCUSSIONS

Bond length and its distortion in the transition metal substituted ZnO have been calculated using universal parameter tight binding approach (Harrison (1980,1981);Kraut and Harrison (1985,1988)). Initially, geometric mean of overlap parameters of group-IV elements corresponding to the periods of Zn and O was used as suggested by Harrison. Bond length of ZnO computed in this way is 1.794Å with an error of 9.94%. Barnowski(1984), Talwar et al(1987) and Sasireka et al(1999) using the same method calculated the bond length of ZnO as 1.75, 1.793 and 1.794 Å respectively. Then we tried other possible modes of overlap parameter. An arithmetic mean of overlap parameters was used in place of the geometric mean. Alongwith this modification, the hybrid energy was computed incorporating 3d-shell energy of Zn which is expected to affect hybridization and hence bonding. This resulted into an improvement in bond length  $d_{ZnO}=1.838\text{\AA}$ . The number of iterations, using Newton-Raphson method, however, remained six as in the earlier case.

We then argued that since the elements exhibit periodic properties, the corresponding periods must have some effect on their physical properties. The weighted average of overlap parameters with carbon-row as one, being the first row to contain a semiconductor, was, therefore, utilized. This led to a drastic improvement in the result in which  $d_{ZnO}=1.970\text{\AA}$  with an error of 1.1%. The number of iterations was also reduced to four. These modifications were then employed in computing bond lengths in V- and Mn- doped ZnO alloys.

Results obtained are given in Table-1.

Table-1

Bond length variation with x in  $Zn_{1-x}M_xO$  (M=V,Mn)

x	Bond length, d (in Å)			
	V		Mn	
	$d_c$	$d_v$	$d_c$	$d_v$
0.01	1.967	1.966	1.966	1.967
0.02	1.965	1.963	1.964	1.963
0.05	1.957	1.952	1.953	1.953
0.10	1.946	1.933	1.937	1.936
0.20	1.923	1.897	1.906	1.901
0.30	1.901	1.860	1.876	1.867
0.40	1.880	1.824	1.850	1.833
0.50	1.860	1.787	1.825	1.798

x=impurity content,  $d_c$ =calculated bond length,  $d_v$ =bond length using Vegard's law.

In case of  $Zn_{1-x}M_xO$  alloys, the volume deformation and charge transfer may be assigned to cause deviation from Vegard's law. Indeed, the presence of d-shells, which have extended lobes, tends to increase the bond length and hence the unit cell volume. On alloying the MO bond is formed partially at the impurity site. The pure M-O has the rock-salt structure, whereas ZnO has the zinc blende or Wurtzite structure. Presence of partial M-O bond, therefore, tends to increase the volume with increasing M-content.

The d-values obtained using Vegard's law are also shown in the table for comparison. Results clearly reveal the departure of d-values from Vegard's law. The deviation of computed d-values from those of Vegard's law increases in

$Zn_{1-x}M_xO$  (M=V,Mn) systems with increasing x. The non-linear dependence of lattice parameters and bulk modulus on composition has been reported in  $MgS_xSe_{1-x}$ ,  $MgS_xTe_{1-x}$  and  $MgSe_xTe_{1-x}$ , and has been attributed to the larger mismatch in the structural parameters of constituent binary compounds (Sajid et al(2012)). In

$Zn_{1-x}M_xO$  (M=transition-metal) nanoparticles also the crucial role dopant type in changing the physical properties of nanoparticles has been reported (Anghel et al (2010)). Paul Joseph and Venkateswaran(2011) have discussed the band gap bowing in  $Zn_{1-x}M_xO$  and attributed the origin of brilliant colours of these systems for  $x = 0.05$  to interatomic transitions between the "3d" transition metal ions that are substituted at the cationic site of ZnO. In the study of influence of cobalt doping on the physical properties of  $Zn_{0.90}Cd_{0.10}S$  nanoparticles, Singhal et al(2010) have found a shift of diffraction peak from the undoped position of the standard sphalerite structure of ZnS. This shift is believed to result from the incorporation of Cd ions into the ZnS lattice, and the larger ionic radius of  $Cd^{2+}$  as compared to that on  $Zn^{2+}$  ( $Cd^{2+} : 0.97\text{\AA}$ ;  $Zn^{2+} : 0.74\text{\AA}$ ). The composition dependence of band gap in the systems  $Zn_{1-x}Cd_xS$  has also been discussed in terms of a bowing parameter. In the magnesium doped ZnO alloys, the lattice constants have been found to follow Vegard's law, whereas the bulk modulus and band gap were found to depend non-linearly on alloy composition x. The energy band gap bowing is primarily due to chemical-charge-transfer effect although there are small contributions from volume deformation and structural relaxation too (Amrani et al(2007)).

In  $Zn_{1-x}M_xO$  ionic sizes of  $V^{2+}$  ( $0.79\text{\AA}$ ) and  $Mn^{2+}$  ( $0.82\text{\AA}$  (high spin state)) being larger than that of  $Zn^{2+}$  ( $0.74\text{\AA}$ ) appear to play a major role in volume deformation. Such effects on band gap have also been reported due to doping of transition metal ions (Anghel et al(2010)) and group IIA metal ion (Fan et al (2008)) in ZnO.

It is interesting to note that although the ionic sizes of  $V^{2+}$  and  $Mn^{2+}$  are larger than that of  $Zn^{2+}$ , the nearest neighbor distance of ZnO in the  $Zn_{1-x}M_xO$  alloys decreases with x. While the exact origin of this unique feature is not known, it may be ascribed to the lower values of nearest neighbor distance in pure VO ( $1.604\text{\AA}$ ) and MnO ( $1.627\text{\AA}$ ) than that in pure ZnO ( $1.97\text{\AA}$ ). This leads to decrease in lattice constant and hence the unit cell volume reduces with x. Surprisingly, the density of M(V,Mn) doped ZnO increases with x although the atomic weights of V(50.94) and Mn(54.94) are lower than that of Zn(65.37). This anomalous behavior might be due to proportionately higher reduction in unit cell volume on doping.

In dealing with the alloy problems, it is, usually assumed that the atoms (ions) are locked at ideal lattice sites and the lattice constants of alloys should vary linearly with composition x obeying Vegard's law. However, the deviations from Vegard's law have been reported in semiconductor alloys both experimentally and theoretically (Fan et al (2008); Liou et al (2005); Brancicio et al (2003); Carrier et al (2005); Labidi et al (2009); Sajid et al (2012); Slimani et al (2009)).

The composition dependence of the calculated bond lengths in  $Zn_{1-x}M_xO$  using modified tight binding approach shows clear departure from Vegard's rule. The non-linearity of composition dependence of bond lengths in  $Zn_{1-x}M_xO$  is shown to obey the quadratic relation using regression analysis:

#### 4. CONCLUSION:

We have utilized tight binding approach with modifications to evaluate bond lengths around the impurity site in  $Zn_{1-x}M_xO$  (M = V, Mn). The composition dependence of bond length has been studied. Deviation from Vegard's law has clearly been shown. This departure has been shown to be non-linear. Role of various factors affecting the deviation has been discussed. The volume (unit cell) deformation has been found to be primarily responsible for the deviation.

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