

## Defect energies in ZnSe

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**Abstract.** Ionic models are commonly used in defect studies in sixfold-coordinated I–VII and II–VI compounds. We discuss the use of models of this type for defects in ZnSe, notably for the cation vacancy centre. We show that methods based on the shell model plus empirical interatomic potentials provide a powerful and important tool, complementary to the commoner studies of defect electronic structure. The new method is particularly effective quantitatively in calculations of (i) energies of closed-shell interstitials, (ii) optical charge-transfer energies, (iii) Stokes shifts, e.g. band gap excesses, (iv) thermodynamic energies, such as internal energies and entropies (though entropies are not calculated in the present paper), and (v) the distortion and polarisation fields near defects needed as a preliminary to fuller studies of electronic structure.

Our specific application to the zinc vacancy centre in ZnSe predicts successfully the nature of the ground state, the mean optical charge-transfer energy, and other properties. We also calculate the energies of Frenkel and Schottky disorder.

### 1. Introduction

The II–VI compounds form in two main types of structure: those which exhibit the close-packed, sixfold coordination, like MgO and NiO, and those which exhibit one of the more open, fourfold-coordinated structures, like ZnO and ZnSe. The structural differences reflect differences in crystal cohesion, and there are several studies of the systematics of structure and its dependence on ionicity, on covalency (both variously defined) and their relative importance.

For the sixfold-coordinated structures, most studies are agreed that an ionic picture is a good first-order description. Such systems would include oxides like MgO and NiO. The properties of the perfect hosts, notably lattice dynamics, elastic and dielectric properties, and thermochemistry, are all satisfactorily described. Quantitative agreement with observed defect energies is also obtained. The ionic approach does not mean covalency is absent. It means instead that covalency is modelled (in part, at least) by the empirical potentials within the ionic model. Those features of covalency not modelled can be added separately, for the important situations are usually easy to identify. Experimental neutron and spin resonance data show that covalency is small, except possibly for interstitial defects, for which there are short interatomic spacings, and for special aspects like covalent contributions to crystal-field splittings.

For the fourfold-coordinated II–VI compounds, the position is much less clear. Both experiments and detailed calculations are less comprehensive. Our present paper tests the extent to which methods used for the sixfold-coordinated systems apply to less-ionic,

fourfold-coordinated crystals. We have two main aims. First, we wish to verify that one can obtain a satisfactory quantitative description of some of the basic defects. Secondly, we show that for what we term 'simple' defects, one can get satisfactory estimates of important defect energies without explicit solution of the Schrödinger equation. We obtain these estimates using a well established defect modelling system based on the Harwell HADES code (Lidiard and Norgett 1972, Norgett 1972). We emphasise that our approach does not give a universal solution of the semiconductor defect problem. It does offer new possibilities in a restricted but important class of problems. Moreover, it can exploit existing codes which treat defects and regions around them far too large for any current or immediately foreseeable methods based directly on the Schrödinger equation. The type of method we use, based on empirical interatomic potentials and polarisabilities (not to be confused with empirical molecular orbital parameters), has been used by several workers for fourfold-coordinated II–VI compounds (Neumark 1980, Harding 1981, Mackrodt *et al* 1980, Walker 1979). We extend this work and discuss it in a broader context.

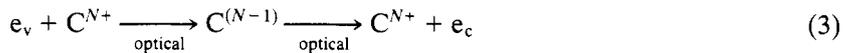
The defects of most interest to us are closed-shell systems, including the alkali interstitials treated previously (Harding 1981). However, any point defect property is acceptable provided that the energy of importance is dominated by the polarisation and distortion of the surrounding lattice, rather than the precise form of a localised defect wavefunction. Thus we can predict charge-transfer energies between different ions A and B:



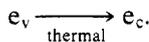
(of which a special case defines the Mott–Hubbard gap:



or the band-gap excess energies in the process involving some defect C:



as opposed to the direct (intrinsic) transition of an electron from the valence to the conduction band:



Clearly, there are some defects we can handle and some we cannot. The cation vacancy  $V^-$  (a hole trapped at an  $M^{2+}$  vacancy; see Schirmer and Schnadt (1976) and Watkins (1972, 1977)) is one we may expect to be able to treat. The anion vacancy  $F^+$  (an electron trapped at an  $X^{2-}$  vacancy), on the other hand, is one where other methods (Harker 1976, Kauffer *et al* 1976) are essential. In this paper we use the  $V^-$  centre as a test case, since there are good experiments, and the predictions are a rather sensitive test of the model assumed.

## 2. The perfect crystal and interatomic potentials

We obtain suitable interatomic potentials by fitting to the known bulk properties of zinc selenide. We take a fully ionic model, based on  $Zn^{2+}$  and  $Se^{2-}$ , and assume that the

**Table 1.** Shell-model parameters.(a) Short-range interactions  $A \exp(-r/\rho) - C/r^6$ 

	$A$ (eV)	$\rho$ (Å)	$C$ (eV Å <sup>-6</sup> )
Zn–Se	2518.7	0.31895	2.0
Se–Se	1238.2	0.34019	10.0

(b) Shell charges and shell–core force constants

$$Y(\text{Zn}) = -8.62|e|, K(\text{Zn}) = 975.0 \text{ eV Å}^{-2}$$

$$Y(\text{Se}) = -2.5|e|, K(\text{Se}) = 6.73 \text{ eV Å}^{-2}$$

short-range part of the interatomic potential may be represented by a function of the form

$$\psi(r) = A \exp(-r/\rho) - C/r^6. \quad (4)$$

Such a form gives an adequate description for the potential except at small  $r$ . Potentials for the short-range Zn–Se and Se–Se interaction were obtained by fitting to the elastic constants  $C_{11}$  and  $C_{12}$  while also requiring the bulk strain on the lattice at the equilibrium spacing to be low (less than 2%). The short-range Zn–Zn interaction was assumed negligible, since the Zn–Zn distance is much larger than the sum of the Pauling radii.

In the shell model, the shell parameters represent the polarisation and distortion of the valence electrons of the ions at the level of a dipole approximation. The sign of the anion shell charge should be negative, but that of the cation could be positive because of overlap polarisation (Bilz *et al* 1975). We fit the shell parameters to the dielectric constants and  $C_{44}$  while requiring the anion shell charge to be negative and both shell charges to be reasonably small. In order to obtain a reasonable value for  $\epsilon_0$ , the atomic polarisabilities of  $\text{Zn}^{2+}$  and  $\text{Se}^{2-}$  have to be rather high. Values calculated from the fitted shell parameters give  $\alpha_{\text{Zn}^{2+}} = 1.1 \text{ Å}^3$ ,  $\alpha_{\text{Se}^{2-}} = 13.5 \text{ Å}^3$ , compared with the Pauling

**Table 2.** Calculated and experimental bulk properties.

Property	Calculation	Experimental	Reference
Elastic constants			
$C_{11}$	$9.08 \times 10^{11} \text{ dyn cm}^{-2}$	$8.72 \times 10^{11} \text{ dyn cm}^{-2}$	Hodges and Irwin (1975)
$C_{12}$	$7.19 \times 10^{11} \text{ dyn cm}^{-2}$	$5.24 \times 10^{11} \text{ dyn cm}^{-2}$	
$C_{44}$	$1.73 \times 10^{11} \text{ dyn cm}^{-2}$	$3.92 \times 10^{11} \text{ dyn cm}^{-2}$	
Dielectric constants			
$\epsilon_0$	7.42	8.80 (0 K)	Strzalkowski <i>et al</i> (1976)
$\epsilon_\infty$	5.60	5.60 (0 K)	Hite <i>et al</i> (1967)
Piezoelectric constant			
$e_{14}$	$-130 \times 10^4 \text{ esu cm}^{-2}$	$1.47 \times 10^4 \text{ esu cm}^{-2}$	Berlincourt <i>et al</i> (1963)
Cohesive energy	-33.85 eV	-37.43 eV	Waddington (1959)
Lattice strain	1.38% ( $a_0 = 5.6676 \text{ Å}$ )		

values (Pauling 1927) of  $\alpha_{\text{Zn}^{2+}} = 0.3 \text{ \AA}^3$ ,  $\alpha_{\text{Se}^{2-}} = 10.6 \text{ \AA}^3$ . Even with these values the fitted  $\epsilon_0$  is low, and so the long-range polarisation will be underestimated. This shows, together with the poor fit to  $C_{44}$  and  $e_{14}$ , that the model we are using is too simple. The main failing is that the model ignores bond-bending forces which will be of importance in ZnSe and will particularly affect  $C_{44}$ . However, the potential does give a reasonable representation of the bulk modulus and dielectric constants, and should therefore give fairly accurate values for defect energies whenever they do not depend sensitively on details of the bonding.

A previous empirical potential has been obtained for ZnSe (Harding 1981); however, this does not give acceptable results for defect energies involving holes binding to vacancies. Both potentials give similar results for Frenkel and Schottky defects showing that, as observed for many systems, the exact form of the interatomic potential is not normally of crucial importance in obtaining reasonable defect energies provided that the required energy involves sums or differences of the HADES calculations.

In some calculations it is necessary to consider different charge states of Zn or Se. In many analogous calculations the difference in short-range interionic potential has been ignored, it being assumed that the only term of importance is the Coulomb term. Here we shall correct for this short-range contribution,  $\delta$ , calculating changes in  $\psi$  by an electron gas method (Harker 1980). Results will be quoted both including this correction (model II) and ignoring it (model I).

### 3. The zinc vacancy centre in ZnSe

#### 3.1. Ionic and covalent descriptions

There are two extreme ways of thinking of ZnSe. One is as a purely ionic system, with  $\text{Zn}^{2+}$  and  $\text{Se}^{2-}$  ions. The other is as a covalent system in which covalent bonds between  $\text{sp}^3$  hybrids are formed; here one has  $\text{Zn}^{2-}$  and  $\text{Se}^{2+}$ . Whatever one's views, it is clearly better to define defect charge states operationally. Thus the zinc vacancy we consider here is that which would be produced by removing a ( $\text{Zn}^+$ ) ion.

We now note (following Stoneham 1975, p 618) that the important features can be described in a strictly parallel way in both the covalent and ionic limits. In the ionic picture one removes both an ion,  $\text{Zn}^{2+}$ , and an electron. The energy is lowest when the hole left is localised on a single Se neighbour (giving an  $\text{Se}^-$  ion), since this optimises the lattice strain and polarisation terms. In the covalent picture one removes an ion,  $\text{Zn}^{2-}$ , and adds three electrons. Removing the ion leaves four  $\text{sp}^3$  hybrid orbitals, each pointing into the vacancy, and each containing one electron. Adding the electrons pairs the electrons in three of the hybrids, leaving a single hole on one of the seleniums. Once lattice relaxation has occurred, one is left with a situation essentially identical in both pictures, with a hole localised on a single selenium, next to the cation vacancy.

#### 3.2. Relation to $V^-$ centres in oxides

It has been stressed, notably by Schirmer (see especially Schirmer and Schnadt 1976) and Watkins (1977) that centres like that obtained by removing  $\text{Zn}^+$  from ZnSe are very similar to the  $V^-$  centres in oxides as well as to the silicon vacancy centres. We support this view, and indeed our quantitative calculations correspond to those for MgO (Norgett *et al* 1977) and other oxides (Harding 1980).

For fourfold coordination, the main features are given by the tight-binding model system of Schirmer and Schnadt. We note these points:

(i) In the ground state, the hole will localise on a single selenium, rather than equally on four neighbours, provided the relaxation energy ( $E_{JT}$  of Schirmer and Schnadt) exceeds  $3J$ , where  $J$  is the resonance integral.

(ii) The optical charge-transfer transitions are ones in which the hole moves from the single selenium to the other three selenium neighbours. Symmetry analysis shows there to be two transitions. One is excited by axially polarised light; this is to the symmetric state with energy  $\frac{8}{3}E_{JT} - 2J$ . The other, to a doubly degenerate state, is induced by light polarised perpendicularly to the defect axis, and occurs at energy  $\frac{8}{3}E_{JT} + J$ .

(iii) there may be also intra-ionic ('crystal-field') transitions involving mainly the single selenium.

Our calculations go slightly beyond this model. The main differences are first that we calculate separately the relaxation energy  $E_{JT}$  and the centroid ( $\frac{8}{3}E_{JT}$ ) of the optical band using a rather more general atomistic model; the ratio  $8/3$  is valid only in somewhat restrictive circumstances. Likewise, the  $J$  which enters the relative stability criterion ((i) above) is actually appropriate to a slightly different relaxed geometry to the  $J$  which enters the optical splitting ((ii) above). The distinction is important here: within the Schirmer–Schnadt model stability of the ground state with localisation on a single neighbour requires the centroid of the optical band to be at an energy greater than  $8/3$  times the energy separation of the two components. The criterion is violated by the experimental values for ZnSe. Further, we shall calculate several observable defect parameters other than those discussed by Schirmer and Schnadt. These include ionisation and capture energies, formation energies, motion energies and response to stress.

One further deduction using the Schirmer model concerns the optical linewidth and its temperature dependence. The full width at half maximum of each band at the lowest temperatures becomes  $2(\ln 2)^{1/2}(\frac{16}{3}E_{JT}\hbar\omega_0)^{1/2}$ , i.e.  $3.8454(E_{JT}\hbar\omega_0)^{1/2}$ . This defines a phonon energy  $\hbar\omega_0$  which also occurs in the factor  $[\coth(\hbar\omega_0/kT)]^{1/2}$  describing the temperature dependence of the width.

### 3.3. Observed and predicted energies

Results are collected in table 3 using each of the potentials described in § 2. We shall concentrate on model II, which we believe to be the most realistic. The results for model I show mainly what a stringent test of a theory is provided by predictions for this type of centre.

Watkins' data give the following information. First, the hole is localised on a single selenium, i.e.

$$E'_{JT} > 3J' \quad (5)$$

where the prime relates to the different geometries involved in the optical and stability expressions discussed earlier. Secondly the two bands observed at 1.4 eV and 2.65 eV have the expected polarisations, and are separated by

$$3J'' = 1.25 \text{ eV}. \quad (6)$$

The centroid of the levels is at

$$\frac{8}{3}E''_{JT} = 2.23 \text{ eV} \quad (7)$$

**Table 3.** Predictions for the  $V^-$  centre.

	Experiment	Theory	
		Model I	Model II
$E'_{JT}$	>1.25 eV from the stability criterion if $J' = J''$	2.79	1.08 eV
$E''_{JT}$	0.84 eV from splitting of optical bands	2.01 eV	0.59 eV
$E^{\circ}_{JT}$	0.45 eV from Stokes shift of $V^{2-} \rightleftharpoons V^- + e_c$		
$J'$	Not known directly		not calculated
$J''$	0.41 eV		not calculated
$\hbar\omega_0$	33 meV from $E'_{JT}$ and linewidth 23 meV from $E''_{JT}$ and linewidth LO phonon frequency 26 meV $\tau_A(X)$ 8.8 meV		
Thermal ionisation energy $V^- \rightarrow V^{2-} + h$	0.7 eV	1.4 eV	1.16 eV
Splitting under stress $eV/\text{\AA}$ symmetrised displacement	1.26 eV $\text{\AA}^{-1}$		0.3 eV $\text{\AA}^{-1}$
Thermal ionisation energy $V^0 \rightarrow V^- + h$	not known	1.07 eV	0.79 eV

allowing for the double degeneracy. The optical linewidth, measured from the figure in Watkins (1971) is about 0.64 eV, whence

$$(E''_{JT}\hbar\omega)^{1/2} \approx 0.17 \text{ eV} \quad (8)$$

with  $\hbar\omega$  the effective phonon frequency. From these experimental data we deduce the values given in table 3.

We note the large difference between  $E'_{JT}$  and  $E''_{JT}$ . Both theory and experiment are consistent with  $E'_{JT}$  being about 50% larger than  $E''_{JT}$ . This is partly because  $E'_{JT}$  includes both electronic and lattice (ionic) polarisation energies, whereas the optical charge transfer only involves changes in the electronic component. In the context of a HADES calculation, the energy  $E'_{JT}$  is the difference in thermal energy (i.e. cores and shells relaxed) between the case where the hole is spread out over the four nearest-neighbour Se atoms and the case where the hole is localised on a single Se.  $E''_{JT}$  is 3/8 of the optical transition energy, calculated as the difference between the ground state and the state in which the hole is distributed on the other three selenium atoms; the shells are allowed to follow the hole in the transition, but the cores remain fixed. We also note how close  $\hbar\omega$  is to the longitudinal optic frequency, i.e. close to what one would have guessed. We also include a recent estimate (Lee *et al* 1980b) of the Jahn–Teller energy obtained from

the Stokes shift in the transitions involving capture of an electron by the  $V^-$  centre. Again, this is a slightly different quantity.

Watkins (1981) has also measured the stress response of the optical absorption, from which is deduced the ground-state splitting  $\delta E$  as a function of (111) stress. It is convenient to describe the results in terms of  $Q$ , the magnitude of the symmetrised combination of displacements of the nearest neighbours as calculated by elasticity theory for stress applied to a perfect ZnSe crystal. The definition of  $Q$  corresponds to  $(Q_\xi + Q_\eta + Q_\zeta)/\sqrt{3}$  in the notation of Larkins and Stoneham (1971). Watkins deduces the following:

$$\partial(\delta E)/\partial Q = 1.26 \text{ eV } \text{\AA}^{-1}$$

whereas we find  $0.3 \text{ eV } \text{\AA}^{-1}$ . This result is not as accurate as the energies of the charge-transfer transitions. The reason is easily understood: the charge-transfer energies are dominated by polarisation, and the relatively accurate predictions reflect the satisfactory values of the dielectric constants in our model. The ground-state splitting under stress, however, depends on some of the same factors as the piezoelectric constant  $e_{14}$ , which is far less well predicted within our model. An improvement in the potentials (e.g. to include some resistance to bond angle changes) would improve both  $e_{14}$  and  $\partial(\delta E)/\partial Q$ .

We may also predict energies for the binding energies in which the  $V^-$  centre captures an electron or a hole:



We have calculated these on the assumption that the hole is a small polaron localised on the  $\text{Se}^{2-}$  (i.e. the hole is regarded as  $\text{Se}^-$  instead of  $\text{Se}^{2-}$ ). In fact the large-polaron form is more stable by an energy  $\Delta_{\text{SL}}$  which is not readily estimated and which we shall leave explicit. In oxides  $\Delta_{\text{SL}}$  appears to be small (Colbourn and Mackrodt 1981), and for ZnSe may be only a few tenths of an eV. Both reactions are exothermic: for (9) the energy given out is  $(1.16 \text{ eV} - \Delta_{\text{SL}})$ , which can be compared with the reported 0.7 eV. For reaction (10) we predict  $(0.79 \text{ eV} - \Delta_{\text{SL}})$ ; no experimental data exist for comparison.

#### 4. Other intrinsic properties, including Frenkel and Schottky disorder

In this section we consider the basic reactions of Schottky disorder, anion and cation Frenkel disorder, and electronic disorder. We shall make two working assumptions: firstly, in the spirit of the ionic model, we shall assume the species involved are  $\text{Zn}^{2+}$  and  $\text{Se}^{2-}$ ; secondly, we recognise the significant covalent contributions to the observed cohesive energy: so, whenever a cohesive energy is used in the energy cycles, we use the theoretical energy obtained with the PLUTO code using the same potentials as in the other energy terms.

##### 4.1. Schottky disorder

Here a  $\text{Zn}^{2+}$  and a  $\text{Se}^{2-}$  are separately moved from the bulk to the surface.

Cation component	3.25 eV
Anion component	3.44 eV
Total	6.69 eV

We may usefully compare these results with those of Van Vechten (1975), who obtains equal individual components of 3.09 eV, and a total Schottky energy of 6.18 eV. His results are strikingly close to ours, though his arguments have an entirely different basis. Van Vechten's results are strictly enthalpies, whereas ours are internal energies, and Van Vechten implies his results are for neutral individual defect components (i.e.  $\text{Zn}^0$  rather than  $\text{Zn}^{2+}$ ), though this assumption does not appear to be essential so long as the Schottky pair is neutral.

#### 4.2. Frenkel disorder

For the cation Frenkel defect, a substitutional  $\text{Zn}^{2+}$  is moved to an interstitial site. There are two obvious inequivalent sites: one (the  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$  site) surrounded by four Se ions, the other ( $\frac{3}{4}\frac{3}{4}\frac{3}{4}$ ) by four Zn ions. The most stable is determined by the balance between the Madelung terms (which favour Se neighbours for Zn) and repulsive terms (which favour Zn neighbours).

We have calculated both cases, and find both factors significant.

##### *Cation Frenkel*

(a) Zn neighbours 7.05 eV    (b) Se neighbours 6.33 eV

##### *Anion Frenkel*

(a) Zn neighbours 5.90 eV    (b) Se neighbours 7.39 eV.

These energies (and the Schottky energies) are sufficiently large that these defects can play no important part in lattice disorder in ZnSe.

#### 4.3. Band-gap excess

Since the polarisation and relaxation energies will depend on the precise atomic nature of the environment, the energy of the sequence (3) depends on the species C through its repulsive interactions and on its environment; it does not depend on ionisation potentials or on the intrinsic band gap. We have calculated the band-gap excess in four cases:

C ≡ Se substitutional	1.66 eV
C ≡ Zn substitutional	3.93 eV
C ≡ Se interstitial, Se neighbours	2.61 eV
C ≡ Se interstitial, Zn neighbours	3.45 eV.

These are quite large energies, comparable with those for MgO and CaO (Stoneham and Sangster 1981).

#### 4.4. Mott–Hubbard gap

There are several contributions to this quantity (see equation (2) and Stoneham and Sangster 1981): Jahn–Teller, crystal-field, ionisation potentials and covalency corrections, together with the polarisation and distortion term which we calculate. The polarisation and distortion contribution for  $2\text{Ni}^{2+} \rightarrow \text{Ni}^+ + \text{Ni}^{3+}$  is  $-9.92$  eV, i.e. this contribution is exothermic; for comparison, values in oxides are  $-11.90$  eV (MgO) and  $-12.79$  eV (CaO) (Stoneham and Sangster 1981). There is a compensating stabilisation, of course. If one were to use free-ion ionisation potentials (Moore 1952), these give a contribution of  $+18.15$  eV, though covalency corrections are necessary. The Jahn–Teller and crystal-field terms are modest. Experimentally, the Mott–Hubbard gap for

ZnSe: Ni<sup>2+</sup> is known to be less than ( $E_{\text{gap}} - 1.0$  eV) i.e. less than about 1.8 eV (Szawelska *et al* 1981). We have already noted three possible sources of error in the calculation. The errors in the calculation of polarisation and distortion are probably less than 1 eV, so presumably the main source of error is in the use of free-ion ionisation potentials, rather than those appropriate for Ni<sup>2+</sup> embedded in a host lattice.

#### 4.5. Antisite defects

In the antisite defect one has either a Zn ion at an Se site or an Se ion at a Zn site. There are three main components in the energy, only one of which can be estimated with significant reliability by our methods.

The first component, clearly outside our present methods, is the covalent bonding term. The second, the Madelung term, is more subtle. In an ionic picture, two different definitions of effective charge appear. One,  $Z$  say, concerns the dipole moment for unit

**Table 4.** Antisite defects

	HADES defect energy (Model II)	Unrelaxed defect energy	Polarisation/distortion energy
Zn <sup>2+</sup> on Se site	11.82 eV	72.35 eV	-60.53 eV
Zn <sup>+</sup> on Se site	19.88 eV	53.13 eV	-33.25 eV
Zn <sup>0</sup> on Se site	20.51 eV	33.9 eV	-13.4 eV
Se <sup>2-</sup> on Zn site	13.29 eV	75.89 eV	-62.6 eV
Se <sup>-</sup> on Zn site	20.04 eV	56.67 eV	-36.63 eV
Se <sup>0</sup> on Zn site	20.71 eV	37.45 eV	-16.74 eV

[Zn <sup>2+</sup> ] <sub>Zn</sub> + [Se <sup>2-</sup> ] <sub>Se</sub> → [Se <sup>2-</sup> ] <sub>Zn</sub> + [Zn <sup>2+</sup> ] <sub>Se</sub>	25.1 eV
→ [Se <sup>-</sup> ] <sub>Zn</sub> + [Zn <sup>+</sup> ] <sub>Se</sub>	39.94 eV
→ [Se <sup>0</sup> ] <sub>Zn</sub> + [Zn <sup>0</sup> ] <sub>Se</sub>	41.30 eV

These reaction energies are HADES energies, uncorrected for ionisation energies

Ionisation potentials for Zn (Moore 1952)	Zn <sup>0</sup> → Zn <sup>+</sup>	9.39 eV
	Zn <sup>+</sup> → Zn <sup>2+</sup>	17.96 eV

We assume that electron affinities for Se are about the same as those for S. These are (Crossley 1964)

S + e → S <sup>-</sup>	-2.07 eV
S <sup>-</sup> + e → S <sup>2-</sup>	+5.51 eV

displacement of an ion; the separate shell and core components are the ones used in our descriptions of lattice dynamic and dielectric properties. The other,  $Z'$  say, enters in the cohesive energy of the perfect rigid lattice, and is determined by the spatial distribution of charge in that case. Most ionic models assume  $Z = Z'$ , since this avoids possible inconsistencies. Such an assumption is not always valid even in ionic systems and covalent bonding will certainly contribute to differences between  $Z$  and  $Z'$ . In the present paper we have fitted  $Z$ . The Madelung part of the antisite formation energy reflects principally  $Z'$ , and this energy contribution may be overestimated in consequence. The third contribution, from lattice distortion and polarisation, is probably more reliably predicted.

The relevant HADES energies for the antisite defects are given in table 4. It is to be noted that the defect energies go in the opposite direction to what one might naively

expect. As the table shows this is due to trends in the polarisation and distortion terms dominating the opposite trend in the Madelung term.

It is helpful, though not especially accurate, to obtain energy estimates for the singly charged and uncharged ions in the antisite positions within a purely ionic model. For this we require the ionisation potentials for Zn and electron affinities for Se. As an estimate we take the free-ion Zn ionisation potentials from Moore (1952) and assume that the Se electron affinities are of the same order as the affinities for sulphur, which may be obtained from the collection of Crossley (1964). This gives energies for the antisite defect pairs as:

$\text{Se}^{2-}$ on Zn site and $\text{Zn}^{2+}$ on Se site	25.1 eV
$\text{Se}^-$ on Zn site and $\text{Zn}^+$ on Se site	16.5 eV
$\text{Se}^0$ on Zn site and $\text{Zn}^0$ on Se site	10.5 eV.

All these energies are large. Even with the considerable uncertainties in the calculation discussed above it seems reasonable to predict that such defects are unlikely to be observed. One can argue that covalent corrections are likely to be of the order of the errors in the crystal cohesive energy, i.e. 3–4 eV; even at this level, there seems no way of bringing our predictions into agreement with Van Vechten's (1980) estimate of 1.9–2.5 eV.

## 5. Discussion

We have now quite a range of results to allow us to assess an ionic model for ZnSe. As we remarked at the outset, it is clear that there are some cases where the model is expected to be weak. Centres where the Schrödinger equation must be solved for a trapped carrier are an obvious example. Also the model might be expected to be unreliable where covalent energies are critical or the absolute value of the Madelung potential important. However in many cases of interest (e.g. Frenkel and Schottky defects, bound hole systems) there may be compensation between various terms in the required energy, so as to give a reliable final result.

The ionic model appears to work well in cases where the defects involve only closed-shell ions (see especially Harding's (1981) work on alkali interstitials) and also gives acceptable results for charge-transfer calculations. Of the various calculations on the  $V^-$  centre only the calculation of the stress coupling coefficient is very sensitive to the ionic assumption through the precise details of the potential, and this is associated with the poor representation of the piezoelectric constant. We may therefore conclude that in a useful, if limited, range of problems, the ionic model can be used to obtain reasonable estimates for defect energies. In this it can be an adjunct to other methods which encounter problems where the ionic model can be used. Indeed, one possible use of our methods is to provide relaxed atomic positions for use in problems in which solution of the Schrödinger equation is necessary.

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