Landau Theory Analysis of Lattice Disorder in the Wurtzite-based Heterovalent Ternary Semiconductors

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Abstract:

The heterovalent ternary semiconductors that are based on the wurtzite lattice are discussed within the framework of Landau theory. It is shown that this system of II-IV-V₂ semiconductors falls into the set of materials that exhibits lattice disorder via antiphase domain formations, characterized by a klassengleiche (k-type) group-subgroup relation between competing phases. The site exchange defect, which consists of two adjacent antisite defects, is identified as the nucleation mechanism of the antiphase domain formations. Inspection of the atomic arrangements that result from site exchange defect formations reveals that the subgroup phase with space group $Pna2_1$ forms antiphase domains within the group phase with space group $Pmc2_1$. The phase with space group $Pmn2_1$ is an intermediate phase. It follows that the system undergoes first order, reconstructive phase transitions between the lower symmetry, low temperature $Pna2_1$ phase and the higher symmetry, high temperature $Pmc2_1$ phase, with a transient mixed phase regime that occurs around the Curie temperature. The order parameter ($\eta$) of the phase transition is assigned to the $c$-plane net polarization vector, and it is shown that the symmetry of the order parameter corresponds to the irreducible representation of the high symmetry point $S$ in the $Pmc2_1$ Brillouin zone at $k = (1/2, 1/2, 0)$. The Landau potential that describes the system is constructed using the International Tables for Crystallography, the Bilbao Crystallographic Server and the resources at stokes.byu.edu. ZnGeN₂ and ZnSnN₂ are discussed in light of this model. This work illustrates the value of using mathematical crystallography in concert with computational physics.
1. Introduction

The heterovalent ternary semiconductors with stoichiometry I-III-VI$_2$ and II-IV-V$_2$ have more complex lattice structures than their binary parent semiconductors, the II-VIs and III-Vs, due to the added degree of freedom in the two-cation sublattices. Solid-state phase transitions have long been observed in the ternaries however fundamental issues such as the mechanism of the transitions and the order of the transitions remain in question [1,2]. It is also not clear if a single behavior manifests throughout the entire set of heterovalent ternary semiconductors, or if different types of behavior manifest in different types of ternaries.

As a consequence of their complexity, crystal defects and lattice disorder have outsized roles in the functional applications of the broad class of ternary semiconductors. Pioneering work carried out in the 1950s and 1960s explored the potential of the ternaries for thermoelectrics because of the low thermal conductivity of many of the ternaries, which results from lattice disorder [3]. This effort advanced the state-of-the-art, AgSbTe$_2$-rich thermoelectric materials such as LAST and TAGS [4-7]. The ternary alloys Cu(In,Ga)Se$_2$ (CIGS) are important thin film photovoltaic materials. The root cause of light conversion efficiency losses in CIGS is nonradiative defect centers thus there has been a tremendous amount of theoretical and experimental work devoted to the study of these defects [8-10]. Multiple experimental and theoretical studies have investigated the roles that point defects [11,12], grain boundaries [13], off-stoichiometry [14,15], metastable defects [12,16], and antiphase domain structure play in CIGS [17]. Recent studies of line and planar defects [18], and the kinetics of defect complex formation and annihilation have further enhanced our picture of these materials [10,19]. Still, researchers have not arrived at consensus on the key defect or defects responsible for nonradiative recombination defect centers.
Solid-state phase transitions also play a critical role in the functional application of CIGS, and the ternaries in general. The phase transition behavior of CuInSe$_2$ was treated using Landau theory by Folmer and Franzen and a phase diagram was constructed for (Cu$_2$Se)$_x$(In$_2$Se$_3$)$_{1-x}$ in the range 0.55>$x$>0.23 [20]. This work highlighted the importance of off-stoichiometry and metal-site vacancies in CuInSe$_2$ and in the functional behavior of CuInSe$_2$-based photovoltaics. Binsma et al. examined CuInS$_2$ and the Cu$_2$S – In$_2$S$_3$ system using differential thermal analysis [21]. McConnell analyzed metal-rich chalcopyrite (CuFeS$_2$) using Landau theory and emphasized the effect of the cool down rate on the resultant polymorph structure [22]. Ryan et al. emphasized the effect of cool down rate in the phase structure of ZnSnP$_2$ [23]. Polymorph domains were directly observed in ZnSnSb$_2$ using electron microscopy by Tengå et al. Phase transitions were also measured using differential thermal analysis [24].

The foundational work on ternary phase transition behavior described above helped enable CIGS technology by establishing crystal growth temperature regimes below the phase transition point. In CuInSe$_2$, the standard growth temperature is around 875 K [25], which is significantly lower than the Curie temperature ($T_C$) which is approximately 1100 K [21,26]. Lower temperature growth regimes lessen the effect of the phase transition on the defect structure of the device [21]. The emergence of relatively new ternary materials calls for similar analyses in order to characterize the relationship between defect structure and the lattice disorder, and to elucidate the functional importance of the phase transition. ZnSnN$_2$ and ZnGeN$_2$ are electronic materials that have attracted interest in recent years, in large part because their alloy band gaps span the visible spectrum [27-34]. ZnSnN$_2$ and ZnGeN$_2$ exhibit dramatic disorder related phenomena in x-ray diffraction and Raman spectra [35,36]. The degree of disorder has been quantified using order parameters based on the x-ray diffraction spectra of ZnSnN$_2$ and ZnGeN$_2$ [37,38]. It has been argued that the lattice disorder results from a mixture of two phases that form probabilistically during growth. It is argued that, at room temperature, the coexistence of the
two phases, with space groups $Pna2_1$ and $Pmc2_1$, results in global disorder in the lattice while local order is largely maintained [36].

In this work, we investigate the interplay of native defects and lattice disorder in the II-IV-V$_2$ wurtzite-based heterovalent ternary semiconductors and propose a lattice disorder model built on a concomitant type of defect complex. It is shown that a Landau theory analysis of the ternary system directs us to the site exchange defect complex as the mechanism of a solid-state phase transition. We analyze the wurtzite-based ZnSnN$_2$ system under the presumption that the low temperature phase is the $Pna2_1$ phase and that the high temperature phase is the second ordered phase with the space group $Pmc2_1$.

2. Methods

a. Group-subgroup analysis of ZnSnN$_2$ and ZnGeN$_2$

We begin by examining the group-subgroup relationship between the $Pmc2_1$ and $Pna2_1$ phases. The $Pmc2_1$ and $Pna2_1$ space groups have a $G > Z1 > H$ group-subgroup relationship where $G = Pmc2_1$ and $H = Pna2_1$ [39,40]. $Z1 = Pmn2_1$ is the intermediate subgroup. The $G > Z1$ group-subgroup relationship is klassengleiche (k-type). The $Z1 > H$ group-subgroup relation is also k-type. The unit cells for the three structures are shown in Fig. 1, along with the Barnighausen tree which describes the structural transformation. Given our choice of axes, the $Pna2_1$ structure is relabeled $Pbn2_1$.

The unit cells of the three structures are shown in Fig. 1. Lahourcade et al. calculate using first principles that the formation energy of the $Pmc2_1$ phase is equal to that of the $Pbn2_1$ phase to within an uncertainty of 10 meV per nitrogen atom [28]. Quayle et al. predict that the formation energy of the $Pmc2_1$ phase is higher than the formation energy of the $Pbn2_1$ phase by only $0.013 \pm 0.003$ eV per formula unit and $0.116 \pm 0.005$ eV per formula unit for ZnSnN$_2$ and ZnGeN$_2$, respectively [36].
The differences in the symmetry properties of the three structures are subtle because the atomic positions of each structure are the same as the wurtzite structure, within an idealized model with no relaxations. Each structure has periodicity along the c-axis determined by a two-fold screw axis rotation \((2\_1)\) (Fig. 1). We assign the origin to the screw axis location, which shifts by \((-\frac{1}{2}, -\frac{1}{3}, 0)\) from \(Pmc2\_1\) to \(Pmn2\_1\). The \(Pmc2\_1\) structure has a glide mirror plane along the \(c\) axis: \(c \rightarrow (x, y, \frac{1}{2} + z)\), which becomes a glide mirror plane with translation along both the \(a\) axis and \(c\) axis: \(n \rightarrow (\frac{1}{2} + x, y, \frac{1}{2} + z)\) in the \(Pmn2\_1\) structure. The mirror plane: \(m \rightarrow (x, y, z)\), in the \(Pmn2\_1\) structure becomes a glide mirror plane: \(b \rightarrow (\frac{1}{2} - x, \frac{1}{2} + y, z)\) in the \(Pbn2\_1\) structure [39].

Structures with a \(k\)-type group-subgroup relationship are characterized by antiphase domain formation [41]. Figure 2 shows a graphical representation of the formation of \(Pmn2\_1\) intermediate phase domains within the \(Pmc2\_1\) phase, and the transformation of the \(Pmn2\_1\) domains to \(Pbn2\_1\) antiphase domains. Fundamental to the construction of the antiphase domains is the site exchange defect, which consists of two adjacent antisite defects, \((II^2_n + IV^{+}_n)\). Starting with Fig. 2a, the green boxes highlight the \(Pmn2\_1\) unit cells. The central blue box highlights the \(Pmc2\_1\) unit cell of the background lattice. The \(Pmc2\_1\) phase is transformed into the \(Pmn2\_1\) phase by the accumulation of site exchange defects. The \(Pmn2\_1\) crystal structure is realized within the \(Pmc2\_1\) background by the sequential exchange in positions of the cations numbered 1-3. Moving to Fig. 2b, the transformation of the \(Pmn2\_1\) domains into \(Pbn2\_1\) domains is realized by the sequential exchange in position of the cations numbered 4-8. To guide the eye, two red lines are drawn on Fig. 2b. At the top of Fig. 2b, the red line traces the characteristic straight-line arrangement of cations in the \(Pmc2\_1\) background lattice. Near the middle of Fig. 2b, the red line that runs through the antiphase domains traces the characteristic zigzag arrangement of cations associated with the \(Pbn2\_1\) phase.
Fig. 1. Barnighausen tree of the ternary nitride system with $G > Z1 > H$ group-subgroup relation. Left: Projection of the $c$ plane of the $Pmc2_1$, $Pmn2_1$, and $Pbn2_1$ crystal structures. Unit cells are outlined in orange. Symmetry operations are based on the IUCR conventions. Lattice parameters in the cell transformations down the center are respective to the unit higher in symmetry. Right: Atomic positions of the three structures.
Fig. 2. Antiphase domains within the $Pmc2_1$ structure. The faint atoms are the $Pmc2_1$ background lattice. The blue boxes highlight the unit cell of the $Pmc2_1$ phase. In the top panel, the green boxes highlight the $Pmn2_1$ unit cell formed by site exchange defects. In the bottom panel, the right side, red box highlights one domain orientation of the $Pbn2_1$ antiphase domain, and the left side, red box highlights the second domain orientation of the $Pbn2_1$ antiphase domain. The two red lines trace the characteristic straight and zigzag cation arrangements of the $Pmc2_1$ and $Pbn2_1$ structures, respectively. The green arrows represent the polarization vectors within the $c$ plane associated with the $Pmc2_1$ and $Pbn2_1$ phases.
The number of domain orientations is given by the index of the group-subgroup relation \( n \),

\[
n = ([|G|]:|H|)(Z_H:Z_G),
\]

where \(|G|\) and \(|H|\) are the orders of the point groups of \( G \) and \( H \), respectively, and \( Z_G \) and \( Z_H \) are the numbers of formula units in the primitive unit cells of \( G \) and \( H \), respectively [42]. The \( G > Z_1 \) relationship has an index of two \( (n = 2) \) meaning that there are two possible domain orientations. This is apparent in Fig. 2a by noting that an equivalent phase domain could be constructed consisting of the opposite colored atoms. This second domain type would result from a different choice in the first exchange defect site. The \( Z_1 > H \) relationship is also \( n = 2 \), making the \( G > Z_1 > H \) relationship \( n = 4 \). Two domain orientations are depicted in the bottom panel of Fig. 2b. The other two domain orientations are essentially the same but with opposite colored atoms.

b. Calculated site exchange defect formation energies

Generally, in the heterovalent ternary semiconductors, the site exchange defect is a low formation energy defect because it is self-compensating and charge-neutral. The formation energy of the site exchange defect has been calculated using first principles for four ternaries and in each case it is the lowest or amongst the lowest formation energy defects. Zhang et al. calculated that the site exchange defect costs 0.65 eV/pair in CuInSe\(_2\) relative to the most stable structure [11]. The site exchange defect was calculated by Zapol et al. to cost 0.13 eV/pair in ZnGeP\(_2\) relative to the most stable structure [43]. In ZnGeN\(_2\), calculations by Skachkov et al. and by Adamski et al. predict values for the site exchange defect of 2.8 eV/pair and 2.05 eV/pair, respectively, relative to the most stable structure [44,45]. The calculations by Skachkov et al. are particularly interesting as they predict that the formation energy per defect pair for an arrangement of two adjacent site exchange defects is 500 meV/pair less than for a
single isolated site exchange defect, indicating that there is an energetic benefit to the coalescence of site exchange defects. In ZnSnN$_2$, the site exchange defect is predicted by Lany et al. to cost approximately 0.04 eV/pair relative to the most stable structure [46].

It must be stated that the relationship between the formation energies quoted above, which were calculated at 0 K, and the more important formation energies at temperatures near the Curie temperatures, which are typically greater than 800 K [1,2], is not well-established. Indeed, in solid-state phase transitions such as the ones discussed here, the Gibbs free energy of the competing low temperature subgroup phase and the high temperature group phase grow closer to one another as the Curie temperature is approached (Fig. 3). Given that the two competing phases and the site exchange defect are directly related, as illustrated in the wurtzite-based ternary structures in Fig. 2, it follows that the difference in Gibbs free energies for the two phases and the site exchange defect formation energy are also directly related. Therefore, if the difference in formation energies of the two competing phases becomes smaller as the Curie temperature is approached, then the formation energy of the site exchange defect relative to the most stable phase will also become smaller.

![Fig. 3. Representation of the Gibbs free energies of the group and subgroup phases.](image)

\[ \Delta G_{\text{cold}} = G_{\text{Group}} - G_{\text{Subgroup}} \]

\[ \Delta G_{\text{hot}} = G_{\text{Group}} - G_{\text{Subgroup}} \]
3. Landau theory treatment of ZnSnN$_2$ and ZnGeN$_2$

a. Identification of the order parameter and active representation

Landau theory provides a powerful tool to investigate solid-state phase transitions. Landau theory is built upon an order parameter ($\eta$) which is an observable and measurable property of the material that is distinct to each phase of the system. The order parameter is finite in value for the low temperature phase, and zero for the high temperature phase above $T_C$. Near the transition point, the value of the order parameter is small which allows for an expansion of the free energy of the system in terms of the order parameter [47]. This expanded free energy - the Landau potential ($\Phi$) - can reveal emergent phenomena near $T_C$. Central to solving for the Landau potential is the identification of the ‘active representation’ which, according to the model of soft mode mediated phase transitions, is the symmetry species of the vibrational mode that drives the phase transition [41,47]. To determine the Landau potential, we first assign a suitable order parameter with symmetry that corresponds to the active representation. From there we make use of the reference tables compiled by Stokes and Hatch and their associated online resource to obtain the Landau potential [48,49].

Like the wurtzite structure, the ZnSnN$_2$ lattice can be viewed as two interpenetrating hexagonal close-packed sublattices; one sublattice consists of N atoms and the other consists of Zn and Sn atoms. Within the two-dimensional c plane, the Zn and Sn cations are positioned on hexagonal lattice sites. The charge interactions between the cations on the two-dimensional hexagonal lattice include an ionic component due to the different valency of the Zn and Sn atoms. We assign the order parameter to the c plane polarization vectors associated with the ionicity. The $Pbn2_1$ phase is characterized by a net polarization vector, which is antiferroelectric in type. This net polarization vector is constructed in the left side domain of Fig. 2b. The four green arrows in the domain represent the polarization vectors and it is apparent that they summate to a finite net polarization vector. The three green arrows in the right
side domain represent three antiferroelectric net polarization vectors. The net polarization for the
*Pmc2₁* phase is zero, as illustrated in the blue box in Fig. 2b.

To determine the symmetry species of the order parameter, we focus attention on the center-
most net polarization vector labeled $\eta$ in the right side red box in Fig. 2b. The vector $\eta$ points along the
same direction as the vector,

$$
\mathbf{r} = (a, b, 0),
$$

where $a$, $b$ is the $a$-lattice parameter, $b$-lattice parameter of the *Pmc2₁* phase, respectively. The vector $\eta$ is proportional to $\mathbf{r}$ in magnitude. The vector $\mathbf{r}$ in reciprocal space is,

$$
\mathbf{g} = \left(\frac{1}{2a}, \frac{1}{2b}, 0\right),
$$

by the relation $r_i g_j = \delta_{ij}$. This wavevector $\mathbf{g}$ is equivalent to the high symmetry point $S$ of the *Pmc2₁*
structure. Thus, the order parameter is associated with the $S$ wavevector at $\mathbf{k} = \left(\frac{1}{2}, \frac{1}{2}, 0\right)$.

To show that the symmetry species of $\eta$ corresponds fully with the $S$ wavevector, we determine
the transformation relations of the two embedded domains, which carry $\eta$ (Fig. 2b). Inspection shows
that the left side domain can be transformed into itself by the identity transformation and by a two-fold
screw axis rotation about the $c$ axis. The left side domain can be transformed into the right side domain
by a mirror plane along the $b$ axis and a glide mirror plane along the $a$ axis. These four transformations
relations are listed in the coset decomposition in Table I. The four transformation relations are
equivalent to the symmetry operations of the *Pmc2₁* space group [50]. The correspondence between $\eta$
and the $S$ wavevector demonstrates that they share an equivalent symmetry species; that the active
representation of this system is the $S$ wavevector irreducible representation.
Table I. The left cosets of the Pmc2₁ subgroup. The left and right sides of the brackets denote the rotational and translation elements of the symmetry operation, respectively. The symmetry operations relate to the unit cell of Pmc2₁, where \( T = n_1 a + n_2 b + n_3 c \), and \( n_1, n_2, \) and \( n_3 \) are integers, and \( a, b, \) and \( c \) are the unit translations of Pmc2₁.

b. Construction of the Landau potential

Now that we have the active representation we can find the Landau potential. The Landau potential is invariant with respect to the symmetry species of the active representation. Thus, \( \Phi(D\eta) = \Phi(\eta) \) where \( \eta'_i = \sum_{j=1}^n D_{ij}\eta_j \) and \( D \) is the set of matrices that form the image of the active representation [48]. Since \( \Phi \) is an invariant function, it is expressed in terms of invariant polynomials. To obtain the invariant polynomials for our system, we simply turn to the internet resource ISOTROPY Software Suite [49]. The Landau potential for our system is given by,

\[
\Phi = \Phi_0 + A\eta^2 + B\eta^4 + C\eta^6, \tag{4}
\]

where the coefficients \( A, B \) and \( C \) are dependent on pressure and temperature. The expansion is carried out to the 6th degree.

The plot of \( \Phi \) versus \( \eta \) in Fig. 4 shows the first order nature of the phase transition under the condition that \( B \) is negative. The solid line in Fig. 4 represents the free energy at the Curie temperature. This potential function is consistent with a system that undergoes a reconstructive phase transition, in which, chemical bonds are broken, atoms are mobile on the lattice and the system is in a mixed phase state consisting of both Pbn2₁ and Pmc2₁ phase domains. Such a phase transition is necessarily first order [41]. It is likely that some degree of the mixed phase state will persist within the lattice upon cooling from the growth temperature, resulting in lattice disorder. The amount of disorder that remains at room temperature is likely dependent on the cooling rate. If the material is quenched, a greater amount of disorder will remain in the lattice at room temperature than if the material is slowly cooled.
Fig. 4. The Landau potential of the wurtzite-based heterovalent ternary semiconductors.

4. Conclusion

The ternary nitrides are emerging functional materials that have potential for multiple technologies in part because they consist of mostly earth-abundant and nontoxic elements, and because of their wide band gaps. The ternary nitrides are one class of materials in an expanding portfolio of functional materials being investigated to meet the technological challenges of the day. Of critical importance to the development of these new technologies is a full understanding of the base materials’ fundamental properties. Mathematical crystallography is a powerful tool that can help reveal the fundamental properties of materials that may exhibit heterogenous nanoscale and mesoscale structure such as the wurtzite-based ternary nitrides [51].
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