Perfect short-range ordered alloy with line-compound-like properties in the ZnSnN$_2$:ZnO system

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We present a new solid-state material phase which is a disordered solid solution but offers many ordered line-compound features. The emergent physical phenomena are rooted in the perfect short-range order which conserves the local octet rule. We model the dual-sublattice-mixed semiconductor alloy (ZnSnN$_2$)$_{1-x}$(ZnO)$_x$, using first-principles calculations, Monte-Carlo simulations with a model Hamiltonian, and an extension of the regular solution model by incorporating short-range order. We demonstrate that this unique solid solution, occurring at a “magic” composition, can provide an electronically pristine character without disorder-induced charge localization and, therefore, a superior carrier transport similar to ordered phases. Interestingly, this phase shows singularities that are absent in the conventional solid-solution models, such as the regular solution and band-gap bowing model. Thermodynamically, this alloy phase has a sharply reduced enthalpy at its composition (like a line compound), but it still requires the entropy from long-range disorder to be stabilized at experimentally accessible temperatures.

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INTRODUCTION

Materials properties depend on composition$^{1,2}$ and atomic arrangement$^{3,4}$. Since the Bronze Age, solid solutions, formed by alloying elements to occupy interstitial or substitutional lattice sites of metal crystals, have been used to increase the mechanical strength. Compared to the pure metal phase, this type of alloying creates local lattice strains that impede dislocation movement$^5$. More recently, solid solutions have become a common protocol in semiconductor$^{11}$, and realizing different topological semimetal phases$^{12}$. In solid solutions, properties of interest can be tuned by alloying elements to occupy interstitial or substitutional lattice sites of metal crystals, have been used to increase the mechanical strength. Compared to the pure metal phase, this type of alloying creates local lattice strains that impede dislocation movement$^5$.

from a solution of a large number of chemical species differing in size, electronegativity, or valence state. With increased chemical complexity, a certain degree of SRO will generally develop as a compromise between strain, chemical bond, and electrostatic energy$^{1,18,19,23}$. Particularly, strong SRO effects must be expected when there are significant attractive forces between the constituents, thereby precluding the use of random alloy models. This is the case, e.g., for the mutually compensating strain fields of III–V alloys with both large- and small-atom mismatch$^{24}$, and for the electrostatic interactions in non-isovalent alloys$^{25,26}$.

SRO in long-range-disordered systems often has a profound effect on the electronic and optical properties$^{6,27-29}$. Thus, we require an order parameter as a measure of the degree of SRO. We note that previously defined SRO parameters based on bond statistics, such as $\xi$ in ref. $^{18}$ and $s$ in ref. $^{30}$, provide only partial SRO information. For example, in (GaN)$_{1-x}$(ZnO)$_x$, a pair of N–Ga$_x$Zn$_{1-x}$ and N–Ga$_x$Zn$_{1-x}$ tetrahedral motifs gives the same number of N–Ga/ N–Zn bonds as two N–Ga$_x$Zn$_{1-x}$ motifs. But they are different from the view of local coordination and, more importantly, energetics$^{29}$. Figure 1 shows a cluster of the wurtzite (ZnSnN$_2$)$_{1-x}$(ZnO)$_x$ system (ZTN0), illustrating the anion-centered N–ZnSn$_x$ and O–ZnSn$_x$ motifs, where $i+j=4$. The ($ij$) distribution of these motifs serves as a measure of SRO and allows for an expansion of the local (SRO) contribution to alloy mixing enthalpy

$$\Delta H_{\text{SRO}} = \frac{1}{N_M} \left( \sum_{ij} e_{ij}^{N}n_{ij}^{N} + \sum_{ij} e_{ij}^{O}n_{ij}^{O} \right),$$

(1)

where $n_{ij}^{N}$ and $n_{ij}^{O}$ are the number of respective N and O centered motifs, $N_M$ is the total number of motifs, and $e_{ij}$ is the energy-expansion parameters, as previously determined in ref. $^{31}$. This model Hamiltonian reflects the local octet rule$^{32-34}$, which can be expressed as $Q_M = q^{N/O} + 1/4 \sum_{ij} (i^2n^j + j^2n_i^j) = 0$, where $Q_M$ is the local charge of a N or O centered motif, and $q = +2$, $+4$, $-3$, $-2$ are the formal oxidation states of Zn, Sn, N, and O, respectively. The octet-rule-conserving N–ZnSn$_x$ and O–ZnSn$_x$ motifs do not contribute to the mixing enthalpy, i.e., $e_{ij}^{+2} = e_{ij}^{+4} = 0$. The energy

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RESULTS

Thermodynamics

We extended the quasi-chemical approach in the regular solid-solution model \(^{(29)}\) to study the thermodynamics of ZTNO solid solutions. Rather than atoms in binary alloys, the building blocks are now formed by the local motif structures. Statistically, this treatment separates the degrees of freedom into the SRO (first shell) and long-range order (LRO, beyond the first shell) parts in the partition function as \(Z = Z_{\text{SRO}}Z_{\text{LRO}}\). Here, \(Z_{\text{SRO}}\) depends on the internal degrees of freedom in the local structure and \(Z_{\text{LRO}}\) relates to the arrangement of motifs. The mixing enthalpy \(\Delta H_{\text{mix}}\) is then expressed by this motif-based regular solid-solution model as

\[
\Delta H_{\text{mix}}(x) = \Delta H_{\text{SRO}} + \Omega x(1-x),
\]

with \(\Delta H_{\text{SRO}}\) as defined in Eq. (1). The term \(\Delta H_{\text{LRO}} = \Omega x(1-x)\) describes the LRO contribution to the mixing enthalpy assuming a random motif distribution. As illustrated in Fig. 1, \(\Delta H_{\text{LRO}}\) is controlled by the arrangement of the anion-centered motifs, i.e., \(Z_{\text{LRO}}\). The motif-interaction parameter can be expressed as \(\Omega = z\Delta e\), where \(z\) is the anion–anion coordination number (\(z = 12\) in the wurtzite lattice). \(\Delta e = e_{\text{NO}} - \frac{1}{2}(e_{\text{NN}} + e_{\text{OO}})\) denotes the differences in motif–motif interactions, in analogy to the bond energies in binary alloys \(^{(30)}\).

The formulation of Eq. (2) allows us to describe the non-random short-range-ordered but long-range disordered ZTNO solid solution. To obtain atomic structure models with realistic degrees of SRO, we performed Monte-Carlo (MC) simulations at fixed compositions using the motif Hamiltonian, i.e., Eq. (1), in 128-atom ZTNO supercells. Random seeds were equilibrated at 5000 K and then cooled at a rate of 6000 MC steps per K. After equilibration at 700 K, a typical growth temperature for thin-film deposition \(^{(47)}\), the structures are relaxed by statistically minimizing the number of octet-rule-breaking motifs, resulting in a minimized \(\Delta H_{\text{SRO}}\). The remaining octet-rule-breaking motifs are due to geometric frustration in non-magic compositions and cannot be removed by further lowering the MC temperature (It should be noted that thin-film growth can result in non-equilibrium disorder described by a higher “effective temperature,” reflecting disorder due to limited kinetics \(^{(57)}\)). For MC equilibrated structures at 700 K, the energies and corresponding mixing enthalpies \(\Delta H_{\text{mix}}\) were calculated from density functional theory (DFT) calculations \(^{(50-52)}\).

Figure 2a shows the DFT-calculated mixing enthalpy of the MC equilibrated structures as a function of composition. Most data points follow the expected quadratic dependence of \(x\), except for the singular points at \(x = 0, 0.25\), and 0.5. For these compositions, we observe PSRO, i.e., only the octet-rule-conserving motifs occur. At \(x = 0\), the PSRO is trivially fulfilled for ZnSnN\(_2\) with its wurtzite crystal structure (space group 33, P6\(_3\)mc); but for \(x = 0.25\) and 0.5, these are non-trivial results from the MC simulation. We then fit \(\Delta H_{\text{mix}}\) of the non-PSRO structures to Eq. (2) and obtain \(\Delta H_{\text{SRO}} = 12.9 \pm 0.9\) meV/motif and \(\Omega = 113.8 \pm 6.3\) meV/motif. Notably, we find for the non-PSRO structures that the contribution from \(\Delta H_{\text{SRO}}\) is in good approximation a constant across the composition range \(0 < x < 0.5\) (see Supplementary Fig. 1), indicating a more or less constant fraction of residual non-ideal motifs. At the “magic” compositions, the MC optimization removes all octet-rule-breaking motifs and \(\Delta H_{\text{SRO}} = 0\). We further performed an exhaustive search over the full composition range in a 64-atom \((2 \times 2 \times 1)\) cell and confirmed that perfect SRO structures occur only at \(x = 0.25\) and 0.5, besides the trivial cases of \(x = 0\) and 1. We note that unlike in other cases of solid solutions and line compounds that show symmetry with respect to composition, e.g., the Ni\(_3\)Al and NiAl\(_2\) phases in the Ni–Al system \(^{(53)}\), this symmetry is here broken due to alloying of a ternary (ZnSnN\(_2\)) and a binary (ZnO) phase. Indeed, the exhaustive search did not reveal a PSRO phase at \(x = 0.75\) on the oxygen-rich side of the
disorder (Exemplary PSRO structure suggesting a considerable residual entropy from long-range three-dimensionally mixed, which was found only for the PSRO we are here interested in the case where the two motif types are While such superlattices could accommodate in principle all octet-rule conserving structure, a minimum concentration of such composition range. As seen in Fig. 2b, the case of $x = 0.5$ is a layered superlattice formed by N–Zn$_2$N$_2$ and O–Zn$_2$Sn$_2$ motifs. While such superlattices could accommodate in principle all compositions via variation of the layer thickness and periodicity, we are here interested in the case where the two motif types are three-dimensionally mixed, which was found only for the PSRO phase at $x = 0.25$. This phase also showed a larger number of configurational representations (see Supplementary Table 1), suggesting a considerable residual entropy from long-range disorder (Exemplary PSRO structure files are available in the Supplementary data 1 to 4).

We can attribute the emergence of this phase at a specific composition to crystallographic “frustration” due to the connectivity of the motif structure within the topology of the underlying wurtzite lattice. For example, in any given octet-rule conserving structure (e.g., $x = 0$ or 1), adding a single charge-conserving (2ON + Zn$_2$Sn) or (2NO + Sn$_2$O) unit immediately creates numerous octet-rule violating motifs in the neighborhood. In order to maintain the octet-rule conserving structure, a minimum concentration of such additions is required in conjunction with a global rearrangement of the ionic distribution on the wurtzite lattice. A comparable phenomenon has led to the identification of extended anti-site defects in chalcogenides. The interest in the PSRO phase at $x = 0.25$ is further motivated from an electronic structure perspective, since either superlattices or O rich compositions are expected to cause charge localization effects that deteriorate electronic properties. Indeed, it is now well established that more dilute N concentrations in ZnO cause defect-like mid-gap states.

The singularity in $\Delta H_{\text{mix}}(x)$ at $x = 0.25$ (Fig. 2a) resembles the situation in a line compound, where a large enthalpy reduction results from crystallization into a crystal structure that accommodates the respective stoichiometry. Despite the large reduction, $\Delta H_{\text{mix}}$ remains positive, implying the phase separation into ZnSnN$_2$ and ZnO at low temperatures. However, at finite temperatures, the minimization of Gibbs free energy ($\Delta G = \Delta H - T \Delta S$) defines the thermodynamic equilibrium of the NpT ensemble. For the PSRO structure to form, there are two critical temperatures: $T_{S_S}$ below which the material tends to be phase-separated, and $T_{S_B}$ above which random structures are thermodynamically preferred. To determine these transitions, we determined $\Delta G$ for the fully random alloy (no SRO) using $\Delta H_{\text{mix}}(0.25) = 149$ meV/motif calculated from DFT and the entropy for random mixing on both sublattices, $\Delta S = 1.16 \text{ kg/motif}$. For estimating the entropy of the PSRO structure, the exact enumeration of configurations becomes impractical at the 128-atom supercell level. We also noticed some well-known methods such as Pauling’s technique are not practical due to the additional complication from two types of tetrahedra, i.e., N–Zn$_2$Sn$_2$ and O–Zn$_2$N$_2$. Instead, we use the N–O two-center 20-motif cluster (Fig. 1) as a model to estimate the entropy from long-range disorder in the presence of PSRO. We enumerate all configurations observing the octet rule while varying $n_O$ and $n_N$ (see Supplementary Fig. 2). A maximum entropy of $\Delta S_{\text{PSRO}} = 8.44 \text{ kg/motif}$ is obtained for the cluster at $n_O/n_N = 3:9$, which locally satisfies the composition $x = 0.25$. The corresponding entropy $\Delta S_{\text{PSRO}} = 0.42 \text{ kg/motif}$ is considerably smaller than the random entropy. In addition, it is worth noting that the enumeration of configurations from small clusters underestimates the total configurational entropy. However, it is sufficient to stabilize the PSRO (ZnSnN$_2$)$_{0.75}$(ZnO)$_{0.5}$ alloy at finite temperatures, given the substantial enthalpy reduction relative to non-PSRO structures. Figure 2c shows the stability of the PSRO phase relative to the phase-separated ($T < T_{S_S}$) and fully random ($T > T_{S_B}$) structures, with a stability range between about 500 and 2100 K. The stabilization temperature of the fully random structure is close to the “effective temperature” that has been inferred in thin-film growth.

Therefore, suitable post-deposition treatments may be necessary in practice to stabilize the PSRO structure at the magic composition.

Electronic structure

The band gap is often sensitive to atomic ordering and distribution. Because the MC relaxed supercells have 128 atoms, direct GW calculations as performed for the primitive cell of ordered ZnSnN$_2$, become impractical. Thus, we used a simplified single-shot hybrid $\pm U$ (SSH $\pm U$) functional to calculate the band structures. The parameters in the SSH $\pm U$ functional were tuned to reproduce the GW results at a small cell level. The calculated band gaps as a function of composition $x$ are shown in Fig. 3. We observe that the PSRO structures at $x = 0.25$ behave very differently from non-PSRO structures, with the band gap falling outside the 3σ band of the band gap bowing model fitted to non-PSRO structures:

$$ E_g = a(1 - x) + E_g^{\text{ZnO}} x - b(x(1 - x)), $$

where we obtained $a = 1.41 \pm 0.07 \text{ eV}$ and the bowing parameter $b = 1.40 \pm 0.14 \text{ eV}$. $E_g^{\text{ZnO}}$ is the wurtzite ZnO band gap ($3.4 \text{ eV}$). Because we are fitting the band gaps of the non-PSRO, we include
the $x = 0$ limit as a free parameter $a$, instead of using the gap of the ordered ZnSnN$_2$ phase. Similar to the behavior in the mixing enthalpy, the band gap shows a singularity at $x = 0.25$, peaking at $E_g = 1.87$ eV, outside of the 3σ band. By eliminating high Zn-coordinated N motifs, such as N–Zn$_2$N$_x$, the PSRO structures experience less hybridization between N–p and Zn–d orbitals. This causes a lower valence band maximum (VBM) and an increased band gap. The band gap extrapolated to $x = 0$ is close to the gap of pure ZnSnN$_2$. This observation reflects the fact that even though the Zn-rich motifs cause an upward bowing of the VBM, they do not cause a defect state inside the gap at low concentrations. At $x = 0.5$, ZTNO forms a ZnSnN$_2$/ZnO superlattice structure, i.e., Fig. 2b. In superlattices, the band gap is somewhat ill-defined because it is formed by two subsystems (see Supplementary Fig. 3).

**Electronic band gap as a function of composition in ZTNO.** Electronic band gap ($E_g$) as a function of composition ($x$): the black dotted line represents fitting according to the gap band bowing model between disordered ZnSnN$_2$ and ZnO. The shaded area denotes the 3σ prediction band from the fitting. The green rectangles are the band gaps of PSRO structures.

**Charge localization in ZTNO.** The calculated inverse participation ratio (IPR) for PSRO and non-PSRO ZTNO structures at $x = 0.25$ with different degree of SRO ($\Delta H_{\text{SRO}}, \text{meV/motif}$). Note that IPR = 1 stands for an ideal charge-delocalized situation and the offsets of each spectrum are for graphical clarity. $n_j$ denotes the fractions of octet-rule-breaking N–Zn$_2$N$_x$ motifs. The IPR of the ordered ZnSnN$_2$ is included for comparison.

**DISCUSSION**

We described a hitherto unrecognized solid-state material phase borne out of a disordered solid solution but having ordered line-compound features. The development of perfect short-range order in the solid solution is responsible for this interesting physical phenomenon. We performed first-principles and Monte-Carlo calculations for the dual-sublattice mixed semiconductor alloy (ZnSnN$_2$)$_{1-x}$(ZnO)$_x$. At a magic composition $x = 0.25$, we obtained this special solid-solution phase, which is predicted to be stable in an experimentally accessible temperature window. Singularities in the mixing enthalpy and the band gap highlight the special character of this phase from both thermodynamic and electronic-structure perspectives. More importantly, charge localization disappears in this unique solid-solution phase, which predicts to be stable in an experimentally accessible temperature window.

**METHODS**

First-principles total-energy calculation

The supercells of ZTNO structures were relaxed using the Vienna ab initio simulation package (VASP) with the projector-augmented-wave implementations for DFT. The ground-state energies of a $2 \times 2 \times 2$ supercell were calculated with a cutoff energy of 380 eV for the plane-wave basis set and in a $2 \times 2 \times 2$ Gamma $k$-point mesh (or similar $k$-point density for smaller cell size). The reference energies of ZnSnN$_2$ and ZnO were calculated from ordered orthorhombic ZnSnN$_2$ (SG 33, Pna2$_1$) and wurtzite ZnO (SG 186, P6$_3$mc). The convergence criteria is that the total energy is smaller than $10^{-5}$ eV/supercell for the electronic steps and the total force on each atom is smaller than 0.02 eV Å$^{-1}$. The generalized-gradient-approximation in the Perdew–Burke–Emzerhof formula was used for the electron exchange and correlation. Due to the fact that the valence band top is affected by the Zn–d shell, a Coulomb potential $(U - J = 6 \text{ eV})$ was applied to Zn–d orbit with the Dudarev approach. The choice of the $U - J$ value is consistent with the literature.
Electronic structure calculation

In the SSH–U approach, we calculate the diagonal matrix elements for the DFT–U wavefunctions without diagonalization. Formally, this is analogous to the common single-shot GW approach, when replacing the self-energy by the scaled nonlocal Fock potential plus the on-site potential $U$. Expressing the composition as $\text{Zn}_a\text{Si}_b\text{N}_c\text{O}_{2d}$, fitting to GW reference calculations yields the hybrid functional scaling factor $\alpha = 0.144 - 0.052x$ and the composition independent $U - J = -4.2$ eV.1 The latter value is somewhat smaller than in DFT–U, because part of the on-site Coulomb interaction is already corrected by the Fock potential.

DATA AVAILABILITY

All data generated or analyzed during this study are included in this published article (and its Supplementary Information files).

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AUTHOR CONTRIBUTIONS
J.P. and S.L. conceived the research. J.P. conducted the first-principles calculations, thermodynamics analysis, and electronic structure calculations. J.C. and J.P. prepared the atomic structures through Monte Carlo simulations. S.L. and A.C.T. supervised the work. J.P. and S.L. wrote the manuscript with contributions from all authors. All authors contributed to this work through periodic discussions. All authors have given approval to the final version of the manuscript.

COMPETING INTERESTS
The authors declare no competing interests.

ADDITIONAL INFORMATION
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