Long-range order instead of phase separation in large lattice-mismatch isovalent *AX-BX* systems

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Large atomic size mismatch between compounds discourages their binding into a common lattice because of the ensuing cost in strain energy. This central paradigm in the theory of isovalent alloys long used to disqualify alloys with highly mismatched components from technological use is clearly broken by the occurrence of stable spontaneous long-range order in mixtures of alkali halides with as much as 40% size mismatch (e.g., LiF-CsF). Our theoretical analysis of these failures uncovered a different design principle for stable alloys: very large atomic size mismatch can lead to spontaneous ordering if the large (small) components have the ability to raise (lower) their coordination number (CN) within the mixed phase. This heuristic design principle has led us to explore via first-principles structure search a few very largely mismatched binary systems whose components have a propensity for CN disproportionation. We find ordered structures for BeO-BaO (37% size mismatch) and BeO-SrO (30%), and ordering in LiCl-KCl (20%), whereas BN-InN (33%) is found to lower its positive formation enthalpy by ~60% when CN disproportionation is allowed. This new design principle could be used to explore phases unsuspected to order by the common paradigm of strain instability.

I. INTRODUCTION

Making *homogeneous* $A_xB_{1-x}X$ alloys from constituent compounds *AX* and *BX* remains at the heart of many technological applications that demand intermediate material properties between those offered by the end-point components.[1] Such homogeneity requires, however, that the normally positive formation enthalpy ΔH of isovalent octet *AX-BX* systems[2–5] be small enough to avoid phase separation at conventional growth temperatures $T < \Delta H / \Delta S$, with ΔS as the mixing entropy. However, alloying of the commonly used isovalent octet components (such as II-VI or III-V or IV-IV semiconductors) leads to ΔH that increases rapidly with the lattice mismatch between the components,[2–5] thus disqualifying the otherwise attractive highly mismatched ($\geq 10\%$) candidate materials (such as GaP-GaSb, ZnO-ZnTe) from being used (other than at the dilute impurity limit).[6] However the experimental observation[7–10] of long-range ordered structures, implying small or even negative ΔH, from highly mismatched (40%) I-VII alkali halide components, such as LiF-RbF or LiF-CsF, is not explained by the classic rules of inorganic chemistry such as hard acids (small-size charge donors) prefer to bind with hard bases (small-size charge acceptors)[11] and exposes a breakdown of a central paradigm in the theory of isovalent alloys.[1–5] We will use this failure here to design stable structures made of constituents with very largely mismatched binary components (even with small electronegativity difference between cationic and anionic species). Starting from first-principles total-energy minimization we first find that low ΔH compounds are possible when the strain accumulated from mixing two highly mismatched components is released through a specific transformation of the bonding topology of the component solids, specifically, from disproportionation of their coordination numbers (CNs). Second, a simple rule based on *exceptions* to the Magnus-Goldschmidt rule of stable CNs of ionic solids[12] is developed to identify those isovalent components for which the naturally occurring CN can be larger (for one) and smaller (for the other) than that predicted from such rule. We

conjecture that combining such components can lead to low-ΔH compounds despite a very large size mismatch. We then examine quantitatively this heuristic design principle using a global space-group optimization approach.[13,14] We explain the surprising spontaneous ordering[10] in BeO-BaO (37% size mismatched) and BeO-SrO (30%) and find ordering in LiCl-KCl (20%), as well as remarkably low ΔH for BN-InN (33%) when CNs disproportionate. This also opens the way for design of previously disqualified highly mismatched compounds.

II. STRAIN RELEASE THROUGH COORDINATION NUMBER DISPROPORTIONATION

Size-mismatch raises ΔH at constant CN but ΔH can be lowered through CN disproportionation. We first examine in Fig. 1 the behavior of the formation enthalpies versus lattice-mismatch of equiatomic systems with a fixed-CN (=6) and structures with varying CNs. Energy minimizations with fixed lattice topology are carried out based on density functional theory.[15] The fixed-CN system is modeled using strain-relaxed 32-atom special quasirandom structures[16] (SQSs) in a cubic unit cell with the symmetries of the underlying rock-salt lattice, whereas the variable-CN structures are relaxed at fixed symmetry in the experimentally observed structures.[7,8] This approach allows us to quantify the effect of increasing lattice-mismatch in the alloys. Figures 1(a) and 1(b) show that, the mixing enthalpy of fixed-CN structures increase rapidly with increasing lattice mismatch, yet the variable-CN structures are stabilized by size mismatch.

In order to understand the factors at play, we decompose the formation enthalpy ΔH into three components[17] forming a fictitious reaction path from the free-bulk compounds to the final alloyed material,

$$\Delta H = \Delta E_{\text{VD}} + \Delta E_{\text{chem}} + \Delta E_{\text{rel}}. \quad (1)$$

The first step [volume deformation (VD)] is to deform the binary compounds (*AX* and *BX*) from their original respec-
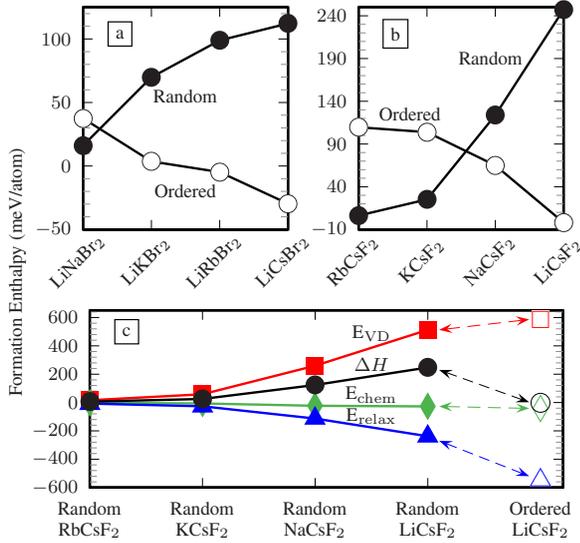
FIG. 1. (Color online) Formation enthalpy of (a) LiMBr$_2$, with M=Na, K, Rb, Cs, (b) MCsF$_2$, with M=Rb, K, Na, Li (increasing lattice mismatch). (c) displays the three components of Eq. (1) for MCsF$_2$ (M=Rb, K, Na, Li) on a fixed-CN (CN=6, random) rock-salt lattice and for the variable-CN (ordered) LiCsF$_2$ structure.

tive equilibrium volumes V_{AX} and V_{BX} to the equilibrium volume $\bar{V}$ (which formally depends on x) of the $A_xB_{1-x}X$ system,

$$\Delta E_{VD} = [xE_{AX}(\bar{V}) + (1-x)E_{BX}(\bar{V})] \\ - [xE_{AX}(V_{AX}) + (1-x)E_{BX}(V_{BX})], \quad (2)$$

where $E_S(V)$ is the energy of system $S=AX$, BX at volume V. In the standard theory[3] of lattice-mismatched alloys, E_{VD} is the dominant term leading to $\Delta H > 0$ and phase separation. The second step (ΔE_{chem}) describes the constant-volume chemical interactions (possibly due to differences in electronegativity and polarizability):

$$\Delta E_{chem} = E_{AX\text{-}BX}^{UR}(\bar{V},x) - [xE_{AX}(\bar{V}) + (1-x)E_{BX}(\bar{V})], \quad (3)$$

where $E_{AX\text{-}BX}^{UR}(\bar{V},x)$ is the unrelaxed (UR) energy at volume $\bar{V}$ of AX-BX with composition x on the fixed (rock-salt) lattice (CN=6) with atoms at the ideal lattice sites. The final step (ΔE_R) allows cell-internal atomic relaxation to reduce strain at constant volume, where the relaxation pathway depends on chemical affinity:

$$\Delta E_{rel} = E_{AX\text{-}BX}^{R}(\bar{V},x) - E_{AX\text{-}BX}^{UR}(\bar{V},x), \quad (4)$$

where $E_{AX\text{-}BX}^{R}(\bar{V},x)$ is the energy at volume $\bar{V}$ of the mixed compound with *relaxed* (R) atomic positions. Figures 1(c) reports the decomposition of Eq. (1) for fixed-CN (random) alloys MCsF$_2$, with M=Rb, K, Na, and Li, as well as for the variable-CN (ordered) structure of LiF-CsF. Whereas different decompositions of ΔH are perhaps possible, Eqs. (1)–(4) offer a clear identification of the factors at play here: (i) consistent with the small difference in electronegativity, the chemical mixing energy ΔE_{chem} is nearly zero for all systems studied here, (ii) in the fixed-CN (random) structures, the

volume deformation energy ΔE_{VD} is indeed the largest positive component of ΔH discouraging bonding, and (iii) accommodation of mismatch through relaxation[18] is insufficient without CN disproportionation. But the CN disproportionation results in a very large release of strain (ΔE_{rel}). Indeed, in the case of ordered LiF-CsF it is sufficient to counteract the volume deformation energy and makes the formation enthalpy negative. This analysis leads us to the conclusion that highly mismatched closed-shell components can bond into ordered structures even for large size mismatch and small chemical affinity under the condition of coordination-number disproportionation.

III. DESIGN PRINCIPLE FOR FORMING COMPOUNDS FROM BINARIES WITH LARGE LATTICE MISMATCH

A closer look at the type of binary octet components,[1–5] which experimentally exhibit $\Delta H_{mix} > 0$, reveals a common feature—they all have same coordination number as their parent compounds, whatever the environments. This observation leads us to develop a heuristic rule for stabilization of systems by very large size mismatch, which can then be examined by first-principles calculations. The basic thinking is as follows. When a system is made of binary components AX and BX of very different natural sizes (molar volumes), the smaller of the two cations experiences a greatly expanded volume within the $A_xB_{1-x}X$ system, and no longer fits snugly in the coordination shell of its parent compound. (Indeed, this often means that it will develop a phonon instability.[19]) If, however, the AX system had the ability to fall back onto a structure with a *lower* coordination number when it occurs in an expanded volume, then it might be stabilized. We thus hypothesize that large size mismatch between octet AX and BX will lead to positive ΔH and phase separation only if the two components do not have the ability to exist in lower and higher coordination numbers, respectively. If, however, the two components are such that their coordination numbers can "disproportionate" (e.g., from n and m to $n-p$ and $m+q$), namely, if the formal reaction

$$AX(CN_n) + BX(CN_m) \rightleftharpoons AX(CN_{n-p}) + BX(CN_{m+q}), \quad (5)$$
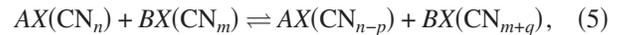
proceeds *forward*, then even large size mismatch might lead to reduced ΔH system and even to long-range ordering (negative ΔH).

To examine which octet binaries have the tendency to alter their CNs, we identify those that tend to violate the classic Magnus-Goldschmidt rule[12] for determining stable CN. This rule predicts from simple geometric arguments the critical ionic radii ratios $\lambda = R_A/R_X$ for which typical closed-packed structures are stable in a given CN. Specifically, CN=4 structures are stable for $0.225 < \lambda < 0.414$, whereas CN=6 structures are stable for $0.414 < \lambda < 0.732$ and CN≥ 8 for $\lambda > 0.732$. Many I-VII, II-VI, and III-V compounds indeed follow this rule (but not all[20]). Figure 2(b) (middle column) illustrates compounds for which Magnus-Goldschmidt rule is correct. Compounds occurring in nature with CN=4, CN=6, and CN=8–12 are illustrated in the bottom, middle, and top rows, respectively. Their ionic radii
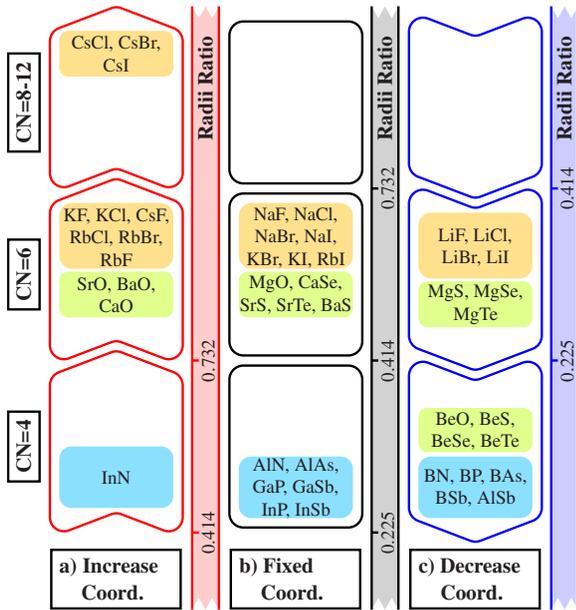
FIG. 2. (Color online) Dependence of coordination numbers (CNs) on the ionic radii ratio. Rows report the coordination number of I-VII, II-VI, and III-V binary closed-shell compounds as they occur in nature. The columns compare these experimental coordination numbers with the predictions of the Magnus-Goldschmidt rule (Ref. [12]): they concur in (b), in (a) empirical evidence show a lower CN, and in (c) a higher CN.

ratios are in the ranges as shown next to each column. Figures 2(a) and 2(c) illustrate compounds which may exhibit a lower (higher) coordination environment than would be expected from the classic thinking. For example, in Fig. 2(a) we show KCl, RbF, CsF, SrO, and BaO naturally occur in rock-salt structure[21] (CN=6), but the model suggests that a *higher* CN>6 is also possible. On the other hand, Fig. 2(c) shows LiCl, LiBr, and LiI which naturally occur in CN=6 but display ionic radii ratios of $\lambda \approx 0.30$, suggesting a *lower* fourfold coordination CN=4. Indeed, they occur with CN=4 in molten salts and gas phase.[22] We conjecture that octet compounds which have the flexibility to change their coordination number to higher [Fig. 2(a)] and lower [Fig. 2(c)] values combine to *AX-BX* systems that can accommodate significant atomic-size mismatch.

IV. *AB INITIO* STRUCTURE PREDICTION OF LARGE LATTICE-MISMATCH COMPOUNDS

Phases made by combining members from Figs. 2(a) and 2(c) may exhibit CN disproportionation and thus lead to complex lattice geometries that cannot be simply inferred from those of the parent compounds. Thus, finding the topology of such emergent structure cannot be accomplished by standard (fixed lattice type) total energy minimizations. We resort to an evolutionary-algorithm approach[14,23,24] which searches for the lowest-energy structure without any a priori knowledge of the lattice vectors or atomic positions based on first-principles calculations.[15] Furthermore, we are interested in finding all lowest-energy structures of combined system $A_{1-x}B_x$ (for instance, A=LiBr and B=CsBr) across the com-

position range $0 \le x \le 1$. The variable-composition general space-group optimization (X-GSGO) (Ref. [24]) allows a *simultaneous* search for any stoichiometry and lattice geometry for structures stable against phase disproportionation.

We ascertain the reliability of the X-GSGO method[25] for the systems at hand by searching for the lowest-energy structures of LiBr-CsBr, known to order.[8,26] We find two nearly degenerate structures (within numerical accuracy) at composition $x=1/2$ have a negative ΔH and are stable against phase disproportionation: (i) the experimentally observed structure,[8] which X-GSGO recovered without any *a priori* knowledge, and (ii) a hitherto unexpected structure.[27] Within the latter structure, the lithium atoms are found in a fourfold coordinated environment, while each Cs atom is surrounded by eight nearest-neighbor Br atoms and two satellite Br atoms. Having verified the ability of X-GSGO to correctly identify known lattices without bias, we attempt to predict unknown low ΔH structures selected via our conjecture. We first apply X-GSGO for LiCl-KCl system, and find a structure[28] at $x=1/2$ with nearly zero formation enthalpy ($\Delta H=2$ meV per atom, e.g., within the numerical accuracy of formation enthalpy calculations). Within this structure, the Li (K) atoms have a fourfold (sevenfold) coordinated environment.

We venture outside the I-VII alkali-halide family and examine the case of BeO-BaO (37% lattice mismatch). Using GSGO, we find a number of structures with variable-CN and negative formation enthalpies. Within a limitation of a 20 atom cell that we use, GSGO reveals only a 50%-50% ordered structure[29] $(BeO)_1(BaO)_1$ with $\Delta H=-42$ meV per atom. Also, BeO-SrO in this structure has $\Delta H=-3.0$ meV per atom. This very low ΔH might be compared with $\Delta H \sim +40$ meV per atom that is expected in normal monoxide combinations like ZnO-MgO[30] or in co-cation II-VI alloys such as ZnS-ZnTe.[31] Fixed-structure first-principles calculations of the experimentally observed structure $(BeO)_5(BaO)_3$ (64-atom cell)[10] also show $\Delta H<0$,[32] as does $(BeO)_3(SrO)_1$.[9] (Unfortunately, X-GSGO for 64-atom cells are currently prohibitively expensive.) The coordination numbers of BeO and BaO in the $(BeO)_1(BaO)_1$ structure are CN=3 and CN=8, respectively, as expected from the expectations from the heuristic design-principle.

We next turned to covalently bonded III-V materials, and examined the BN-InN system having a size mismatch of 33% by first-principles calculations. If one keeps the CN fixed (CN=4) the lowest-energy configuration[33] is the $(AX)_2(BX)_2$ (201) superlattice, also called chalcopyrite, with a computed $\Delta H=+335$ meV/atom. The random alloy $B_{0.5}In_{0.5}N$ has $\Delta H=+610$ meV/atom. Yet when we allow the CN to change, in line with our conjecture that BN can reduce its CN and InN can increase its CN, we find a much lower $\Delta H=+148$ meV/atom relative to BN (CN=4, zinc blend) and InN (CN=4, wurtzite). This enormous energy-lowering relative to the standard expectations based on size-mismatch scaling highlights the breakdown of the latter paradigm in alloy theory.

V. CONCLUSION

The appearance of ordered structures in alloys of closed-shell compounds with large lattice mismatch is unexpected if

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one refers to the conventional understanding that weak chemical affinity between the compounds in conjunction with strain from the mismatched atomic sizes will results in a positive formation enthalpy. However we have shown that for large enough mismatch, a reorganization of the coordination shells can lead to a negative formation enthalpy. The main result of our a Rapid Communication is a design principle predicting ordering and low formation enthalpies in alloys between unsuspected highly mismatched compounds. It has led to explore a few highly mismatched binary systems using GSGO. We find ordered structures for BeO-BaO and BeO-SrO and ordering in LiCl-KCl. Furthermore, we predict very low formation enthalpy in BN-InN. This design principle could be used to explore phases unsuspected to order by the common paradigm of strain instability.

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[25] The structure-search with X-GSGO were performed for structures with less than 20 atoms. The population size is set to 16, and the two worst individuals are replaced by offspring at each generation. The rate of crossover versus mutation is set to 0.7. A minimum of two independent evolutionary runs with 16 or more generations are performed for each GSGO search.

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[28] $(LiCl)_1(KCl)_1$ structure parameters ($Cmc2_1$): $a=4.1$ Å, $b=14.0$ Å, $c=7.3$ Å, Li $(4a)$ at $(0,0.11,0.87)$, K $(4a)$ at $(0, 0.62, 0.40)$, Cl $(4a)$ at $(0, 0.01, 0.14)$, and Cl $(4a)$ at $(0, 0.70, 0.84)$.

[29] $(BeO)_1(BaO)_1$ structure parameters ($P2_1/m$): $a=3.9$ Å, $b=5.3$ Å, $c=5.9$ Å, $\beta=98°$, Be $(2e)$ at $(0.55,1/4,0.87)$, Ba $(2e)$ at $(0.15,1/4,0.31)$, O $(2e)$ at $(0.69,1/4,0.64)$, and O $(2b)$ at $(1/2,0,0)$.

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