Evolution of Alloy Properties with Long-Range Order

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We present a general theory of compounds with partial long-range order. We derive a simple formula that determines the properties of a partially ordered compound from those of the perfectly random alloy and the fully ordered compound. The formula makes accurate predictions of both formation energies and electronic band structures. We also use the formula to predict the band gaps of $\mathrm{Al}_{1-x}\mathrm{Ga}_x\mathrm{As/GaAs}$ superlattices.

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Most alloys are neither perfectly ordered nor perfectly random. Deviations from perfect randomness show up as either short-range order (SRO) or long-range order (LRO). In short-range order [1] atoms are preferentially surrounded either by like atoms ("clustering") or unlike atoms ("anticlustering"), but there are no long-range correlations among atoms. Long-range order is manifested by extra crystallographic diffraction spots ("superlattice spots"); in metals it causes changes in resistivity and specific heat, while in semiconductors it alters the optical properties [2, 3]. Compound-forming alloys exhibit perfect LRO, with LRO parameter $\eta = 1$, only at very low temperatures and under careful growth conditions; imperfect LRO, with $0 < \eta < 1$, is far more common. While electronic structure theories are well developed for perfectly ordered crystals and for random alloys, very little theoretical work has been done for partial LRO [4, 5].

We develop here a general formalism for describing alloy properties as a function of the long-range order parameter η. It can be used in conjunction with first-principles electronic-structure methods, bridging the gap between prior *ab initio* theories for perfectly random alloys ($\eta = 0$) and fully ordered compounds ($\eta = 1$). We derive from this theory a simple formula that describes the properties of a compound with $0 < \eta < 1$ in terms of the properties of the random $\eta = 0$ and perfectly ordered $\eta = 1$ compounds. This allows for a simple interpolation of experimental or calculated data for $\eta = 0$ and $\eta = 1$. We illustrate the accuracy of this formula by reproducing the results of direct 2000-atom supercell calculations, and of first-principles band structure calculations for partial LRO. Since all alloy superlattices can be viewed as instances of LRO, we can also use our formula to predict their band gaps from data on bulk alloys and pure superlattices.

We describe the substitutional $A_{1-x}B_x$ system by way of a generalized Ising model. A particular ordered configuration σ is determined by the occupation of each of the N sites of the lattice with either an A atom or a B atom, assigning an Ising spin variable of $\hat{S}_i = -1$ to sites occupied by A atoms, and $\hat{S}_i = +1$ to those occupied by B atoms. The lattice sites can be grouped into a set of figures with k vertices, where $k = 1, 2, 3$ are single site, pair, and triangle figures. For each class F of symmetry-equivalent figures (e.g., all nearest-neighbor pairs) and for each configuration σ, we define a "correlation function" as the average of the spin products of all figures in the class:

$$\bar{\Pi}_F(\sigma) = (1/\mathcal{O}_F) \sum_f \hat{S}_{i_1}(\sigma)\hat{S}_{i_2}(\sigma)\cdots\hat{S}_{i_k}(\sigma) , \qquad (1)$$

where f runs over the $\mathcal{O}_F$ figures of class F, and the spin product is taken over the k sites of f. Any lattice property $P(\sigma)$ can be rigorously expanded as a series of the complete orthonormal functions $\bar{\Pi}_F(\sigma)$:

$$P(\sigma) = \sum_F \mathcal{O}_F \, p_F \, \bar{\Pi}_F(\sigma) , \qquad (2)$$

where p_F is the contribution of F to property P. The dominant values of p_F may be deduced from electronic structure calculations for a small set of ordered structures. This set of p_F may then be used to calculate $P(\sigma)$, e.g., total energies [6] and band gaps [7], for any other structure.

The random $A_{1-x}B_x$ alloy ($\eta = 0$) is treated by averaging over all possible configurations of $A_{1-x}B_x$. The spins of the random alloy must be completely uncorrelated, so the average of the spin products is $\langle \hat{S}_i\hat{S}_j \rangle = \langle \hat{S}_i \rangle^2$, where the site average of the spins is $\langle \hat{S}_i \rangle = -1\times(1-x)+1\times x = 2x - 1$. Thus for a figure with k vertices,

$$\bar{\Pi}_F(\eta = 0) = \langle \hat{S}_i \rangle^k = (2x - 1)^k . \qquad (3)$$

The physical properties of the random alloy are given by using Eq. (3) in Eq. (2). Even though the site occupations of the random alloy are uncorrelated, this does not imply that the physical properties, such as charge transfer [8] and magnetic moments [9], of individual sites are independent of their local environment [8]. The site-only coherent potential approximation (S-CPA) neglects these correlations, leading to unphysical results, such as Madelung energy of zero for the random alloy (as discussed in Ref. [8]). These local effects in the random alloy can be included in two ways: (a) Construct a giant supercell whose sites are occupied randomly [10, 11], or (b) construct a smaller "special" structure σ_s whose correlation functions $\bar{\Pi}_F(\sigma_s)$ match those of Eq. (3) for the first few, physically important figures [12]. In either approach properties can be calculated using electronic-structure methods. The first approach is statistically accurate but is feasible only when a simplified electronic structure method is used. The second approach, the "special quasirandom structure" (SQS) method [12], results in supercells containing $\lesssim 20$ atoms—small enough to be easily treated using first-principles electronic-structure methods. It closely reproduces the results of ~ 2000 atom supercell calculations where both the supercell and the SQS calculations were performed with the tight-binding [10] or the valence force-field (VFF) methods [11]. We now extend these methods to $0 < \eta < 1$.

A system with partial LRO is defined with respect to a particular fully ordered structure. For example, an $A_{0.5}B_{0.5}$ alloy may have partial ordering of the CuAu-I ($L1_0$) type. In the perfect $L1_0$ structure, layers of pure A and pure B are stacked alternately along the [001] direction of an fcc lattice. An $A_{0.5}B_{0.5}$ alloy with partial $L1_0$ ordering has two distinct types of sites: A-rich and B-rich sites which, in the perfect $L1_0$ structure, would be occupied by A atoms and B atoms, respectively. Assuming that the atoms on the A-rich sites are randomly distributed (and similarly for the B-rich sites), the properties of the partially ordered $A_{0.5}B_{0.5}$ structure are determined by the average spin over all of the A-rich sites $\langle \hat{S}_A \rangle = -\eta$, and the average spin over all of the B-rich sites $\langle \hat{S}_B \rangle = \eta$; more compactly, $\langle \hat{S}_i(\eta) \rangle = \eta \hat{S}_i(L1_0)$, where the index i runs over the two sites of the perfect $L1_0$ unit cell. It follows that the correlation functions for the partially ordered $L1_0$ structure are $\bar{\Pi}_F(\eta) = \eta^k \bar{\Pi}_F(L1_0)$. These results will apply to any type of ordering so long as both the alloy and the perfectly ordered structure have composition $x = 1/2$.

To generalize to the case of composition $x \neq 1/2$, we write the spin average as

$$\langle \hat{S}_i(x,\eta) \rangle = (2x-1) + \eta \sum_{\mathbf{k}\neq 0} S(\mathbf{k},\sigma) e^{i\mathbf{k}\cdot\mathbf{R}_i} , \qquad (4)$$

where σ is the ordered reference structure. Here the sum runs over the Brillouin zone (BZ) of the underlying lattice and $S(\mathbf{k},\sigma)$ is the Fourier transform of the spin variables of the perfectly ordered structure; it is nonzero only at a small set of points. To simplify Eq. (4), note that for the ordered reference structure of composition X_σ (which may differ from x)

$$\hat{S}_i(\sigma) = (2X_\sigma - 1) + \sum_{\mathbf{k}\neq 0} S(\mathbf{k},\sigma) e^{i\mathbf{k}\cdot\mathbf{R}_i} , \qquad (5)$$

using $S(\mathbf{0},\sigma) = 2X_\sigma - 1$. Combining Eqs. (4) and (5) gives

$$\langle \hat{S}_i(x,\eta) \rangle = (2x-1) + \eta[\hat{S}_i(\sigma) - (2X_\sigma - 1)] . \qquad (6)$$

The degree of ordering is limited by the requirement that $|\langle \hat{S}_i(x,\eta) \rangle| \leq 1$, which by use of Eq. (6) implies that (for $\eta \geq 0$)

$$\eta \leq x/X_\sigma \quad \text{and} \quad \eta \leq (1-x)/(1-X_\sigma) . \qquad (7)$$

Perfect ordering ($\eta = 1$) is possible only when $x = X_\sigma$. We can use Eq. (6) to derive the correlation function for any pair figure F

$$\bar{\Pi}_F(x,\eta) = (2x-1)^2 + \eta^2 \left[\bar{\Pi}_F(\sigma) - (2X_\sigma - 1)^2\right] . \qquad (8)$$

In deriving this equation, we assume that the distribution of atoms over the A-rich sublattice, and separately, the distribution of atoms over the B-rich sublattice, are random. This assumption, however, does not imply that we neglect short-range order. Because of the different concentrations of atoms on the two types of sites, the Cowley SRO parameters, defined [1] as $\alpha_F = \left[\bar{\Pi}_F - (2x-1)^2\right] / [4x(1-x)]$, are related [13] by Eq. (8) to the SRO parameters of the perfectly ordered structure: $\alpha_F(x,\eta) = \alpha_F(\sigma)\eta^2 X_\sigma(1-X_\sigma)/[x(1-x)]$.

Our results permit a straightforward generalization of methods (a) and (b) described above for the random alloy to the case of alloys with any degree of LRO. We can perform direct calculations on a giant supercell whose sites are occupied randomly, but in accordance with Eq. (6). The SQS method may be generalized by finding a special structure σ_s whose correlation functions match those of Eq. (8) for the first few figures. A third method is obtained by combining Eqs. (2), (3), and (8) to the description of property P:

$$P(x,\eta) = P(x,0) + \eta^2 \left[P(X_\sigma,1) - P(X_\sigma,0)\right] , \qquad (9)$$

provided that the property can be expressed in terms of single site and pair interactions only. Here $P(X_\sigma,1)$ is the property of the perfectly ordered structure, and $P(x,0)$ and $P(X_\sigma,0)$ are the properties of the random alloy at compositions x and X_σ. A similar equation was noted empirically [4, 5] in the context of the S-CPA. For the common $X_\sigma = 1/2$ reference structures, which are symmetric with respect to $A \leftrightarrow B$ atom interchanges, any ground-state physical property of the $x = 1/2$ alloy must be symmetric with respect to the transformation $\eta \to -\eta$, so that corrections to Eq. (9) must be $O(\eta^4)$; these corrections are due to four-body and higher figures. A simple analysis shows that the maximum error caused by dropping the η^4 contribution is $|a_4|/4$ where a_4, the coefficient of η^4, is a sum of four-body terms from Eq. (2); since experience with the cluster expansion [6–8] shows that four-body interactions are much weaker than the pair interactions, we expect Eq. (9) to be an excellent approximation. Certain electronic energy differences (such as the X_1-X_3 energy difference in the zinc-blende BZ), however, are antisymmetric with respect to $A \leftrightarrow B$ interchange; these should be *odd* functions of η. When applying Eq. (9) to these energy differences, η^2 must be replaced by η [14], and the corrections, due to three-

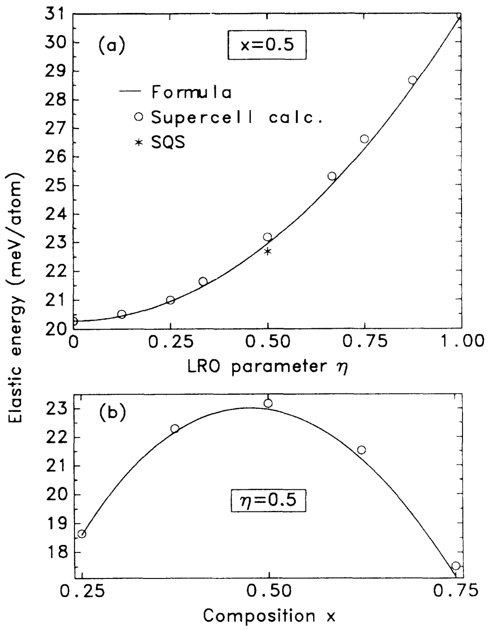

FIG. 1. (a) VFF elastic energies for $Ga_{0.5}In_{0.5}P$ with $L1_1$ LRO as a function of order parameter η. The circles are calculations on large supercells, the asterisk is the result for SQS ($\eta = 1/2$), and the solid curve is the prediction of the simple formula of Eq. (9). (b) Elastic energies for $Ga_{1-x}In_xP$ with $L1_1$ LRO parameter $\eta = 1/2$ as a function of composition x.

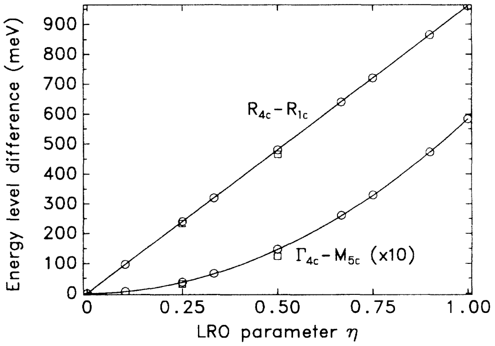

FIG. 2. Pseudopotential electron energy differences for an $Al_{1-x}Ga_xAs$ for $x = 1/2$ and $x = 1/4$ with $L1_0$ LRO and order parameter η. Points are pseudopotential results (circles for $x = 1/2$ and squares for $x = 1/4$), and the solid curves (which are independent of x) are predictions of Eq. (9), using an η^2 dependence for $\bar{\Gamma}_{4c}$-$\bar{M}_{5c}$ and an η dependence for $\bar{R}_{4c}$-$\bar{R}_{1c}$.

body interactions, are $O(\eta^3)$. For alloys with $x \neq 1/2$, the inversion symmetry is lost and the leading-order corrections are due to either three-body interactions (for symmetric properties) or pair interactions (for antisymmetric properties); in these cases we expect the formula to be less accurate than at $x = 1/2$ [15].

We illustrate the application of these three methods in a calculation of the elastic energy of a $Ga_{0.5}In_{0.5}P$ alloy with $L1_1$ (CuPt) LRO, using the VFF model [16]. The giant supercell method is executed in a 2048-atom cell (1920 atoms for $\eta = 1/3$ and 2/3) where the cation sites are occupied randomly in a way consistent with Eq. (6), using a series of different values of $\eta(L1_1)$. The elastic energy is minimized by relaxing all of the atomic positions; relaxation is substantial, lowering the energy of the ordered $L1_1$ structure by 57%. The results are averaged over 20–30 configurations for each value of η; the standard error of the energy estimate is < 0.05 meV/atom. Figure 1(a) shows these results, along with the predictions of Eq. (9), using only the VFF results for $\eta = 0$ and $\eta = 1$. The simple formula is seen to work extremely well. Figure 1(b) shows that the formula works equally well as the composition is varied. The generalized SQS method is executed by finding the periodic structure with eight cations whose pair correlation functions most closely match those of Eq. (8) for $\eta = 1/2$; this structure is an A_2BABAB_2 superlattice in the [133] direction. Its formation energy is shown as an asterisk in Fig. 1(a).

As a second illustration, we calculate the direct band gap of the imperfectly ordered $L1_1$ structure of $Ga_{0.5}In_{0.5}P$ using the linearized-augmented-plane-wave method (LAPW) and the local-density approximation (LDA). We find $E_g = 0.86$ eV for the SQS ($\eta = 0$), and $E_g = 0.55$ eV for the ordered $\eta = 1$ $L1_1$ structure. Using the $\eta = 0$ and $\eta = 1$ results as input to Eq. (9), our formula predicts a band gap of 0.78 eV for $\eta = 1/2$. This compares well with the calculated band gap of 0.76 eV for the 8-cation SQS ($\eta = 1/2$) cell. We also calculated the mixing enthalpies ΔH at $x = 1/2$ using LAPW. We find $\Delta H(\eta = 0) = 79$ and $\Delta H(\eta = 1) = 144$ meV/4-atoms. Using these values in Eq. (9) predicts $\Delta H(\eta = 1/2) = 86$, in close agreement with the direct SQS ($\eta = 1/2$) result of 89 meV/4-atom.

We have also applied the formula to the band structure of $Al_{0.5}Ga_{0.5}As$ and $Al_{0.25}Ga_{0.75}As$ with partial $L1_0$ LRO. Calculations are performed using the pseudopotential plane-wave method and the LDA; we use the virtual crystal approximation for each layer of the partially ordered structures and for the random alloy. Since the splittings are zero for the random alloy, they are predicted by the formula to be independent of x. Figure 2 shows the results for two energy band differences in the $L1_0$ structure. The first, $\bar{\Gamma}_{4c}$-$\bar{M}_{5c}$, belongs to the symmetric representation of the space group, and therefore is well represented by Eq. (9). The second, $\bar{R}_{4c}$-$\bar{R}_{1c}$, is odd with respect to Al↔Ga atom interchanges and, as a result, η^2 must be replaced by η in Eq. (9). In either case, our simple formula makes excellent predictions; as expected the formula is more accurate for $x = 1/2$ than for $x = 1/4$.

Any alloy superlattice can be viewed as a special case of partial LRO. For example, we can apply Eq. (9) to an $(Al_{1-y}Ga_yAs)_p/(Al_{1-y'}Ga_{y'}As)_p$ superlattice, where

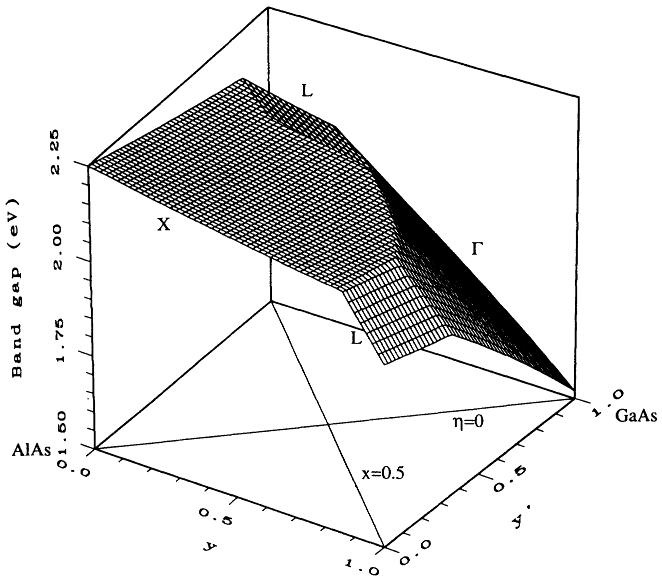

FIG. 3. Predictions for the minimum-energy band gap (in eV) of a $(\mathrm{Al}_{1-y}\mathrm{Ga}_y\mathrm{As})_1/(\mathrm{Al}_{1-y'}\mathrm{Ga}_{y'}\mathrm{As})_1$ superlattice using Eq. (9).

$x = (y + y')/2$, $\eta = y' - y$, and the ordered reference structure is $\sigma = (\mathrm{AlAs})_p/(\mathrm{GaAs})_p$, with $X_\sigma = 1/2$. Such alloy superlattices are often grown intentionally, but may also occur unintentionally in the growth of monolayer AlAs/GaAs superlattices, if the layers are intermixed. Figure 3 shows the predicted minimum-energy band gap for the monolayer [001] superlattice, over the entire range of compositions $\{y, y'\}$. These predictions are made by combining Eq. (9) with the experimental dependence of the Γ, X, and L gaps of the $\mathrm{Al}_{1-x}\mathrm{Ga}_x\mathrm{As}$ random alloy [17] and LDA-band-gap-corrected (using the average difference between the LDA and experimental gaps for GaAs and AlAs) pseudopotential calculations for the gaps of the perfect $(\mathrm{AlAs})_1/(\mathrm{GaAs})_1$ superlattice. The line marked $\eta = 0$ in the figure corresponds to the random alloy as the composition is changed from AlAs to GaAs. Along this line we have the well-known Γ-X crossover of the conduction-band minimum (CBM). The $x = 0.5$ line represents equal concentrations of Al and Ga for different values of the order parameter—ranging from the random alloy ($\eta = 0$) at the center to the perfect monolayer superlattice ($\eta = 1$) at opposite corners. Along this line, the CBM changes from the X point in the random alloy to the L point, with the crossover occurring near $\eta = 0.7$. This X-L crossover has important experimental consequences, since it will lead to an X-like CBM in $(\mathrm{AlAs})_1/(\mathrm{GaAs})_1$ if the interfaces are not sufficiently abrupt [18].

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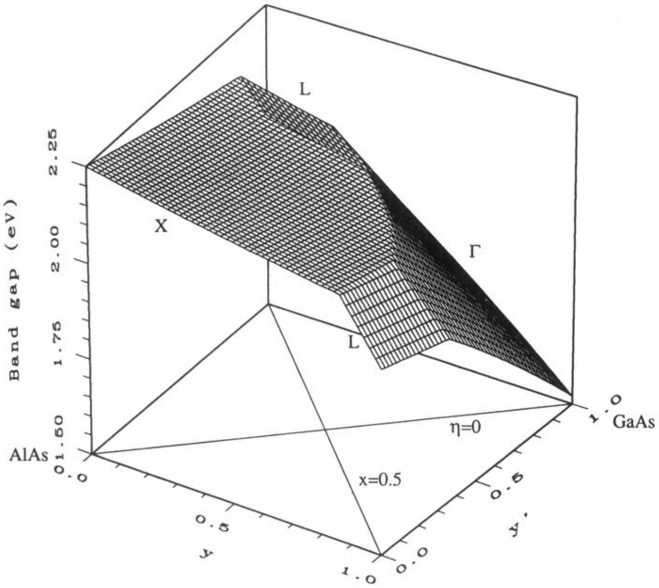

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