Special Quasirandom Structures

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Structural models used in calculations of properties of substitutionally random $A_{1-x}B_x$ alloys are usually constructed by randomly occupying each of the N sites of a periodic cell by A or B. We show that it is possible to design "special quasirandom structures" (SQS's) that mimic for small N (even $N=8$) the first few, physically most relevant radial correlation functions of a perfectly random structure far better than the standard technique does. We demonstrate the usefulness of these SQS's by calculating optical and thermodynamic properties of a number of semiconductor alloys in the local-density formalism.

One of the significant realizations to emerge from recent electronic structure calculations of crystals, impurities, and surfaces[1] is that electronic properties sensitively reflect the details of the microscopic atomic arrangements, including small changes in atomic positions ("relaxation"). Yet, many theories of substitutional $A_{1-x}B_x$ random alloys[2] are nonstructural, in that they consider only the average occupations by $\langle A \rangle$ or $\langle B \rangle$ of *sites*, removing from the theory the informational content associated with the *geometrical arrangements* of atoms around a site. Such is the "virtual-crystal approximation"[2] (VCA), where the alloy is assumed to have a single, $\langle AB \rangle$-averaged type of site, or the site coherent-potential approximation[2] (SCPA), where all A's and separately all B's are assumed equivalent and each is embedded in a structureless *uniform* average medium; structural relaxation is excluded in both approaches. Experimental techniques capable of probing the average *local* properties of alloys[3] have, however, clearly demonstrated the important role played by the microscopic atomic structure. For example, even in homogeneous $A_{1-x}B_x$ alloys without short- or long-range order the average A-A, A-B, and B-B distances are generally different;[3] in semiconductor alloys similar atomic relaxations have been shown to control the band gaps[4(a),4(b)] and thermodynamic[4(c),4(d)] quantities. On the other hand, the obvious difficulty with *structural* theories of alloys arises from the fact that even in the simplest case of a binary system with N sites, there are 2^N possible atomic configurations whose total energy needs to be structurally relaxed, then averaged. One then proceeds in practice either by selecting a smaller number of "representative" configurations (e.g., the Monte Carlo approach[5]), or a single periodic structure with a random distribution of A and B atoms on its N sites.[6] While these techniques explicitly specify the alloy structure, and can hence incorporate atomic relaxation, they approach the statistical limit as slowly as $N^{-1/2}$. Therefore, they involve a rather large number of configurations (e.g., $\sim 10^6$ in Monte Carlo studies[5]) or large cell sizes (e.g., $> 10^3$ atoms) (Refs. 5 and 6), for which first-principles self-consistent calculations (currently restricted to $N \leq 50$ atoms[1]) are still impractical.

We show here that by *selective* occupation of the N lattice sites by A and B atoms one can construct *special* periodic "quasirandom structures" that mimic, for finite N, the correlation functions of an infinite substitutional random alloy far more closely than does the standard approach of occupying each of the N sites randomly by A or B. While both approaches produce the same results for $N \rightarrow \infty$, the present approach produces excellent approximations already for $N=0(10)$, and hence affords application of accurate electronic structure methods[1] for calculating structural, optical, and thermodynamic properties of random alloys. This is illustrated here for a number of semiconductor alloys.

Describing random alloys by *periodic* structures will clearly introduce spurious correlations beyond a certain distance ("periodicity errors"). However, many physical properties of solids are characterized by microscopic length scales that can be ordered according to size to form a hierarchy. For example, interactions between distant neighbors generally contribute less to the total energy than do interactions between close neighbors.[7] We hence guide our construction of "special quasirandom structures" (SQS's) by the principle of close reproduction of the perfectly random network for the first few shells around a given site, deferring periodicity errors to more distant neighbors. This approach has an obvious resemblance to the principle guiding the selection of "special k points" for Brillouin-zone integration.[8]

We characterize the structure of the alloy by the multisite correlation functions familiar from statistical lattice theories.[9,10] Here, any given arrangement of A and B atoms on a lattice (a "configuration" σ) is discretized into its component "figures" $f=(k,m)$, e.g., pairs of atoms (a figure with $k=2$ vertices separated by an mth-neighbor distance), triangles ($k=3$ vertices), etc. Using the language of Ising models,[5,9,10] we assign to each site i in a figure a spin variable $\hat{S}_i$ which takes the value -1 if it is occupied by A, or $+1$ if occupied by B. We define as $\Pi_f(l,\sigma)$ the product $\prod \hat{S}_i$ of spin variables for figure f positioned in the lattice at location l (where l includes also its orientation). There are D_f figures per site. A lattice average (denoted by a bar) of the spin product

over all locations of symmetry-related figures of type f gives

$$\bar{\Pi}_f(\sigma) = \frac{1}{ND_f} \sum_l \Pi_f(l,\sigma). \tag{1}$$

The ensemble average of a physical property P over configurations (denoted by angular brackets) can be rigorously[10] expanded as

$$\langle P \rangle = \sum_{k,m} D_{k,m} \langle \bar{\Pi}_{k,m} \rangle p_{k,m}, \tag{2}$$

where $p_{k,m}$ are the "interaction parameters" of figures $f = (k,m)$ and $\langle \bar{\Pi}_{k,m} \rangle$ are the correlation functions. N_S values of $\{p_{k,m}\}$ can be determined if N_S values of $\langle P \rangle$ are available (e.g., from band theory[7,11]). For a perfectly random (R) $A_{1-x}B_x$ structure, the many-body $(k \neq 0)$ correlation functions are $\langle \bar{\Pi}_{k,m} \rangle_R = (2x-1)^k$; hence, at $x = \frac{1}{2}$, they vanish to all orders, except $\bar{\Pi}_{0,1} = 1$.

The usual approach for simulating properties of random alloys through a finite-N representation of Eq. (2) (e.g., see Ref. 6) assumes that each site should be individually occupied at random by A or B. The extent to which this approach produces a finite-N-atom/cell structure that, as a whole, approaches randomness can be measured by the standard deviation $\eta_{k,m}(N) = |\langle \bar{\Pi}_{k,m}^2 \rangle|^{1/2}$. While for an isolated cell with N lattice site, $\eta_{k,m}^{(i)}(N) = (D_{k,m}N)^{-1/2}$, application of this procedure to a periodic N-atom/cell structure typical of the sizes for which first-principles electronic structure calculations are practical, could produce even larger errors.

This is seen in Table I, which gives for $x = \frac{1}{2}$ the standard deviation $\eta_{k,m}(N)$ obtained by randomly occupying N fcc sites of a periodic structure in a sufficiently large number of ways (~ 3000) so that converged statistics are obtained. We see that $\eta_{k,m}(N) > \eta_{k,m}^{(i)}(N)$ and that periodicity errors (denoted in Table I by correlation function values of ~ 1 rather than 0) occur at rather short distances from the origin.

Our central idea here is that instead of attempting to approach $\langle \bar{\Pi}_{k,m} \rangle_R$ by statistical sampling methods, we can design "special" N-atom periodic structures S whose distinct (i.e., no ensemble average) correlation functions $\bar{\Pi}_{k,m}(S)$ best match the ensemble averages $\langle \bar{\Pi}_{k,m} \rangle_R$ of the random alloy. Since by Eqs. (1) and (2) the error in the property P relative to that in a perfectly random alloy is represented in terms of a hierarchy of distances,

$$\langle P \rangle_R - P(S) = \sum_{k,m}{}' D_{k,m}[(2x-1)^k - \bar{\Pi}_{k,m}(S)] p_{k,m}, \tag{3}$$

(the prime denotes omission of $k = 0$ and 1), it is natural to select the structure S so that the right-hand side is minimized in a hierarchical manner. For instance, insisting that the most important correlation functions — those for the first and second neighbors — have zero errors at $x = \frac{1}{2}$, gives already for $N = 8$ in fcc symmetry an SQS (denoted in Table I SQS-8). Its unit cell is best described as an $A_2B_3A_2B_1$ superlattice along the [113] direction. Using, for example, the criterion that $\bar{\Pi}_{2,1} = 0$ and $\bar{\Pi}_{2,2}^2 + \bar{\Pi}_{2,3}^2 + \bar{\Pi}_{2,4}^2 = \text{minimum}$, we also find that the

TABLE I. The upper part gives the absolute values of the mth-neighbor pair-correlation functions as obtained in SQS; for the perfectly random alloys at $x = \frac{1}{2}$, $\langle \bar{\Pi}_{k,m} \rangle = 0$, hence departure from zero measures errors. Below those we give the standard deviation, also about zero, as obtained in random site-by-site occupations of N atom supercells. Finally, we give the average number of neighbors to a given atom of opposite type.

Atoms/cell	Shell D_j	1st 6	2nd 3	3rd 12	4th 6	5th 12	6th 4
			Errors in correlation functions				
CuPt		0	1	0	1	0	1
SQS-2		0.333	1	0.333	1	0.333	1
SQS-4		0	0.333	0	0.333	0	1
SQS-6		0	0.111	0.333	0.111	0.333	0.333
SQS-8		0	0	0.042	0.083	0.083	0
$N = 8$[d]		0.215	0.504	0.215	1[d]	0.215	0.504
$N = 16$[b]		0.102	0.206	0.102	0.206	0.102	1[d]
$N = 32$[c]		0.073	0.146	0.074	0.146	0.073	0.249
$N = 64$[d]		0.051	0.073	0.035	0.073	0.051	0.127
$N = 108$[c]		0.039	0.054	0.028	0.039	0.039	0.048
$N = 125$[a]		0.037	0.051	0.026	0.037	0.026	0.045
$N = 128$[b]		0.036	0.051	0.026	0.036	0.025	0.062
			Number of neighbors of opposite type				
SQS-8		6 ± 1.8	3 ± 0.5	11.5 ± 1.1	6.5 ± 0.5	11 ± 1.4	4 ± 1
Random		6 ± 1.7	3 ± 1.2	12 ± 2.4	6 ± 1.7	12 ± 2.4	4 ± 1.4

[a]fcc-type unit cell.
[b]bcc-type unit cell.
[c]Simple-cubic-type unit cell.
[d]Periodicity error: $\langle \bar{\Pi}_{k,m} \rangle = 1$, instead of zero.

SQS-4 is an A_2B_2 superlattice along [110], while SQS-6 is an $A_1B_1A_2B_2$ superlattice along [331]. Table I gives for completeness also SQS-2. Although $N=2$ is generally too small to represent a random alloy, we find that the CuAuI structure gives the best overall $N=2$ representation for a random alloy. For each SQS we give in Table I the absolute value of the correlation functions, $|\bar{\Pi}_{k,m}|$; their departure from zero reflects errors relative to an infinite, perfectly random alloy. It is seen that SQS-8 is an excellent choice, equivalent to $N \to \infty$ for the first- and second-neighbor correlation functions (as well as for sixth), to $N=64$ for third neighbors, etc. Its many-body correlation functions (note shown in Table I) also exhibit small values; e.g., the averaged value of $\bar{\Pi}_{3,m}=0$, $\bar{\Pi}_{4,1}=0$, and $\bar{\Pi}_{4,2}=0.167$. As a further measure of the accuracy with which the SQS's represent a perfectly random, infinite structure we give in Table I the number $\langle O_m \rangle$ of mth-order neighbors to a given site that are of the opposite type. In a perfectly random structure $\langle O_m \rangle = D_m \pm (D_m/2)^{1/2}$. The SQS-8 reproduces this distribution within the standard deviations.

Unlike the SCPA or the VCA, the SQS exhibits a *distribution* of local environments of inequivalent A (or B) atoms; hence, when treated by conventional band-structure methods one can simply incorporate in them realistic atomic relaxations and charge redistributions. Unlike cluster-expansion methods,[7,11] [Eq. (2)], the SQS approach is capable of depicting directly the electronic charge distribution in a random alloy and does not require evaluation of $p_{k,m}$ from a truncated expansion.[7,11]

We have applied self-consistently the local-density formalism, as implemented by the linear augmented-plane-wave[12] (LAPW) and nonlocal pseudopotential[13] band-structure methods to a range of pseudobinary $A_{0.5}B_{0.5}C$ semiconductor SQS's. Here, the C atoms reside on the

nominally common sublattice (so the actual number of atoms per cell is $2N$); all A, B, and C atomic positions are allowed to relax (without atomic interchanges) so as to minimize the total energy. A direct band-structure calculation of the total energy of a structurally relaxed SQS (taken with respect to the energies of the binary constituents AC and BC at equilibrium) approximates the excess energy $\Delta H(x=\frac{1}{2})$ of a random alloy. Such direct calculations for SQS-2 and SQS-4 are compared[14] in Table II to results obtained by the cluster expansion. The latter are given by our recent solutions[7] of the three-dimensional fcc Ising model [Eq. (2)], using a converged set of up to fourth neighbor and four-body interactions [$p_{k,m}$ in Eq. (2)]. The interaction energies were obtained by fitting the separately calculated total energies of eight simple periodic structures.[7] Table II shows that a single calculation even on SQS-4 reproduces well, without resorting to statistical calculations, the corresponding results obtained from the full statistical-mechanics simulation: The latter agrees well with measured excess enthalpies.[7,14] For $GaP_{0.5}As_{0.5}$ and $Al_{0.5}Ga_{0.5}As$ we have also calculated, using the pseudopotential method,[13] the properties of SQS-2, -4, and -8. For $GaP_{0.5}As_{0.5}$ we find the relaxed mixing enthalpies $\Delta H = 26.1$, 13.9, and 16.5 meV/(4 atoms) for $N=2$, 4, and 8, respectively (the experimental value[7] is $\sim 18 \pm 10$ meV). For $Al_{0.5}Ga_{0.5}As$ we find 13.7, 10.5, and 10.5 meV/(4 atoms) showing even more rapid convergence.

It is less obvious that band gaps would converge rapidly in Eq. (2). To examine this we have used the pseudopotential calculated direct band gaps $[E_g(S)]$ of N_S ordered structures[7] of $Al_nGa_mAs_{n+m}$, obtaining through Eq. (2) the N_S expansion coefficient $\{p_{k,m}\}$ for $P=E_g$. These were then used to *predict* E_g for a *different* struc-

TABLE II. Mixing enthalpies ΔH [in (1 meV)/(4 atoms)] and optical bowing b of the direct band gaps at Γ (in eV) as obtained by LAPW calculations on $x=\frac{1}{2}$ SQS's. For comparison, we also give $\Delta H(x=\frac{1}{2})$ at $T=800$ K and at $T \to \infty$ (random alloy) as calculated from an Ising model (Ref. 7), and the observed (expt. l) bowing parameters (Ref. 14). SQS-4* denotes results obtained after averaging the crystal-field split states at the valence-band maximum.

	AlAs GaAs	GaSb GaAs	InAs GaAs	GaP InP	HgTe CdTe	ZnTe CdTe	HgTe ZnTe
$\Delta H \frac{1}{2}$							
CuPt	7.5	132	108.5	155.4	9.8	103.5	103.3
SQS-2	11.5	115	66.7	91.0	12.1	54.2	42.5
SQS-4	6.0	80	47.3	73.0	9.8	56.1	49.1
Ising							
$(T=800)$	6.5	86	51.0	66.6	8.2	49.7	40.8
$(T=\infty)$	6.6	91	58.8	81.5	8.4	55.3	47.6
$b(\Gamma)$							
CuPt	1.45	3.25	1.81	1.82	0.49	0.65	0.77
SQS-2	0.61	1.30	0.66	1.08	0.09	0.44	0.45
SQS-4	0.12	0.98	0.51	0.80	0.02	0.40	0.32
SQS-4*	0.10	0.64	0.43	0.62	0.01	0.35	0.20
Expt. l	0.0–0.37	1.0–1.2	0.32–0.61	0.65	0.0–0.23	0.26	0.14

ture (SQS-8). Using $N_S = 5$, 6, and 7, we predict E_g (SQS-8) = 1.42, 1.34, and 1.37 eV, respectively, showing rather rapid convergence, despite the fact that $E_g(S)$ of the starting structures span a large range, between 0.7 and 2.2 eV. A *direct* band calculation on SQS-8 gives $E_g = 1.38$ eV, in excellent agreement with the cluster expansion to sixth neighbors (1.37 eV). Additional convergence tests with $N_s = 27$, to be published separately, confirm that SQS-8 predicts the gaps for GaAlAs and GaAsP to within -0.05 eV or better. Given this success, we have calculated the relativistic band structures of the SQS's for the seven semiconductor alloys using the LAPW method. Table II gives the optical bowing coefficient $b = 4[\bar{E}_g(\frac{1}{2}) - E_g(\frac{1}{2})]$ of the direct alloy band gap at composition $x = \frac{1}{2}$ (where $\bar{E}_g$ denotes the concentration-weighted band gap of the binary constituents; note that due to the difference taken in b, the local-density error cancels to first order). For comparison, we also give the calculated results for the CuPt structure and experimental data[14] for the disordered alloy. Using the pseudopotential method, we find for $GaP_{0.5}As_{0.5}$ the crystal-field–averaged bowing coefficient of the direct gap (in eV) of 0.14, 0.19, and 0.19 for SQS-2, -4, and -8, respectively (the experimental value[14] is 0.21 eV). We see that parameter-free self-consistent calculations on the SQS-N converges well and reproduces the experimental trends. It is important to note that neglect of structural relaxation (as done in VCA and SCPA methods[2]) leads to huge errors in size-mismatched alloys, e.g., we find that b(SQS-2) for unrelaxed Ga_2SbAs is 0.32 eV, instead of 1.30 eV for the relaxed structure and that ΔH is 237 meV instead of 115 meV. For GaAsP, ΔH is 60.2 meV instead of 16.5 meV.

As a final demonstration of the usefulness of the SQS concept we quote its recent application[15] to the study of the optical properties of the $Al_{1-x}Ga_xAs$ alloy. We have constructed a periodic model[15] of this alloy at the $\sim 50\%$-50% composition by populating randomly a 2304-atom unit cell by Ga and Al (As resides on a separate sublattice). The energy levels were then calculated within a tight-binding Hamiltonian whose matrix elements were fitted to the band structure of GaAs and AlAs. A spectral weight analysis of the solutions of the 2304-atom cell produced the alloy band gaps (given in eV, with respect to the valence-band maximum):

$$2.215 \ (\Gamma_{1c}), \quad 2.185 \ (L_{1c}), \quad 2.145 \ (X_{1c}),$$
$$2.645 \ (X_{3c}) \quad (2304 \ \text{atoms}) .$$

Using SQS-8 with just 16 atoms and the same tight-binding Hamiltonian yielded the following band gaps:

$$2.217 \ (\Gamma_{1c}), \quad 2.196 \ (L_{1c}), \quad 2.160 \ (X_{1c}),$$
$$2.640 \ (X_{3c}) \quad (16 \ \text{atoms}) ,$$

i.e., within 0.015 eV of the 2304-atom/cell calculation.

Notice that the band gap of $AlGaAs_2$ strongly depends on its crystal structure (Table II); hence the success of the SQS is significant. This example illustrates the fact that the SQS is also useful in describing optical properties near threshold although it has artificial long-range order.

While the SQS idea was demonstrated to work only for semiconductor alloys, it can be easily generalized to other compositions or lattice types (bcc, diamondlike) and open the way for extending the application of first-principles electronic structure techniques to a variety of metal and semiconductor alloys.

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