Structure and Thermodynamics of Si_xGe_{1-x} Alloys from *Ab Initio* Monte Carlo Simulations

Stefano de Gironcoli and Paolo Giannozzi
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), PHB-Ecublens, CH-1015, Lausanne, Switzerland

Stefano Baroni
Scuola Internazionale Superiore di Studi Avanzati (SISSA), Strada Costiera 11, I-34014 Trieste, Italy

(Received 20 November 1990)

Si_xGe_{1-x} alloys are studied with a new method based on density-functional theory and Monte Carlo sampling. Using perturbation theory with respect to the virtual crystal, we are able to map the alloy onto a lattice gas with long-range interactions, which are determined from first principles. Monte Carlo simulations show that Si_xGe_{1-x} is a model random alloy with a miscibility gap below ≈ 170 K. The bond-length distribution displays three well-defined peaks whose positions depend on composition, but not on temperature. The resulting lattice parameter follows Vegard's law very closely.

PACS numbers: 61.55.Hg, 64.75.+g, 71.10.+x

One of the standard ways of studying finite-temperature properties of solid solutions is to map the alloy problem onto a lattice-gas (or Ising) model, whose coupling constants are usually fitted to some empirically known structural or thermodynamic properties.[1] This approach has received a sound theoretical basis in the "renormalized interactions method" (RIM).[2] In RIM interatomic interactions are fitted to the results of first-principles density-functional-theory (DFT) calculations for some ordered structures which can be described by small supercells, and the resulting statistical-mechanical problem is treated by the cluster-variation method.

In this paper we follow a different but related approach by pursuing an idea previously applied to the electronic structure of semiconductor heterojunctions.[3] The alloy is considered as a perturbation with respect to a periodic virtual crystal, and treated using linear-response theory (LRT). This allows us to map the problem onto a lattice-gas model with only two-body interactions, the mapping being *exact* up to second order in the perturbation. For the sake of clarity, we focus on Si_xGe_{1-x}, the generalization to other semiconductor alloys being straightforward.

The thermodynamics of the alloy is determined by the relative energy of different microscopic configurations. Each of them can be described by a set of Ising-like variables $\{\sigma_{\mathbf{R}}\}$, where $\{\mathbf{R}\}$ are the equilibrium lattice positions of the diamond lattice, and $\sigma_{\mathbf{R}}=+1$ if the ion sitting at $\mathbf{R}$ is Si, and $\sigma_{\mathbf{R}}=-1$ if it is Ge. The formation of the alloy in a given configuration $\{\sigma_{\mathbf{R}}\}$ at molar volume Ω can be conveniently split into three steps: (i) First, the proper amounts of pure silicon and germanium are brought from their equilibrium volumes—Ω_{Si} and Ω_{Ge}—to the desired final volume—Ω—paying an *elastic energy*

$$\Delta E_{\text{elast}}(x,\Omega)=x[E_{Si}(\Omega)-E_{Si}(\Omega_{Si})]+(1-x)[E_{Ge}(\Omega)-E_{Ge}(\Omega_{Ge})]\,, \qquad (1)$$

where $x=\frac{1}{2}(\langle\sigma\rangle+1)$ is the Si concentration. This step is independent of the microscopic configuration, and the elastic energy is easily obtained from bulk equations of state. (ii) The alloy is then formed by placing ions at the *ideal* positions of a diamond lattice with molar volume Ω, according to the prescribed distribution $\{\sigma_{\mathbf{R}}\}$. This step costs a *chemical energy*

$$\Delta E_{\text{chem}}(\{\sigma_{\mathbf{R}}\},\Omega)=E(\{\sigma_{\mathbf{R}}\},\text{ideal},\Omega)-[xE_{Si}(\Omega)+(1-x)E_{Ge}(\Omega)]\,. \qquad (2)$$

(iii) Finally, the atoms are allowed to relax to their equilibrium positions, thus gaining a *relaxation energy*

$$\Delta E_{\text{relax}}=E(\{\sigma_{\mathbf{R}}\},\{\mathbf{u}_{\mathbf{R}}\},\Omega)-E(\{\sigma_{\mathbf{R}}\},\text{ideal},\Omega)\,, \qquad (3)$$

where $\mathbf{u}_{\mathbf{R}}$ is the ionic displacement of the atom sitting at $\mathbf{R}$, due to lattice relaxation. The formation energy of the alloy in a given configuration is the sum of these three contributions. The last two depend on the microscopic arrangement of atoms, and they are therefore the difficult part of the calculation.

Owing to the small chemical differences between Si and Ge atoms, an actual configuration of Si_xGe_{1-x} can be conveniently described as a perturbation with respect to a periodic virtual crystal ⟨SiGe⟩, whose ionic pseudopotential is the average between those of pure Si and Ge:

$$V_{\langle SiGe\rangle}(\mathbf{r})=\sum_{\mathbf{R}}v(\mathbf{r}-\mathbf{R})\,,$$

where $v(\mathbf{r})=\frac{1}{2}[v_{Si}(\mathbf{r})+v_{Ge}(\mathbf{r})]$, and v_{Si} and v_{Ge} are the ionic pseudopotentials of Si and Ge. In the same spirit, displacements from ideal positions are treated by perturbation theory. For any microscopic configuration $\{\sigma_{\mathbf{R}}\}$ and displacement pattern $\{\mathbf{u}_{\mathbf{R}}\}$, the bare perturbing potential is

$$\Delta V(\mathbf{r})=\sum_{\mathbf{R}}\sigma_{\mathbf{R}}\Delta v(\mathbf{r}-\mathbf{R})+\sum_{\mathbf{R}}\mathbf{u}_{\mathbf{R}}\cdot\frac{\partial v}{\partial\mathbf{R}}(\mathbf{r}-\mathbf{R})\,,$$

where $\Delta v(\mathbf{r})=\frac{1}{2}[v_{Si}(\mathbf{r})-v_{Ge}(\mathbf{r})]$. The equilibrium values of $\{\mathbf{u}_{\mathbf{R}}\}$ are to leading order linear in Δv, and higher-order terms are neglected. Up to second order in the perturbation, the energy of the alloy is then given by

$$E(\{\sigma_{\mathbf{R}}\},\{\mathbf{u}_{\mathbf{R}}\},\Omega)=E_{\langle \mathrm{SiGe}\rangle}+\int \Delta V(\mathbf{r})n_{\langle \mathrm{SiGe}\rangle}(\mathbf{r})d\mathbf{r}+\tfrac{1}{2}\int \Delta V(\mathbf{r})\Delta n_V(\mathbf{r})d\mathbf{r}+\mathcal{O}(\Delta v^3)\,, \tag{4}$$

where $E_{\langle \mathrm{SiGe}\rangle}$ and $n_{\langle \mathrm{SiGe}\rangle}(\mathbf{r})$ are the energy and electron density distributions of the virtual crystal—calculated at volume Ω—and Δn_V is the electron charge density linearly induced by ΔV. Using linearity and translational invariance, Eq. (4) can be rewritten as

$$\begin{aligned}E(\{\sigma_{\mathbf{R}}\},\{\mathbf{u}_{\mathbf{R}}\},\Omega)=E_{\langle \mathrm{SiGe}\rangle}+K\sum_{\mathbf{R}}\sigma_{\mathbf{R}}+\tfrac{1}{2}\sum_{\mathbf{R},\mathbf{R}'}J(\mathbf{R}-\mathbf{R}')\sigma_{\mathbf{R}}\sigma_{\mathbf{R}'}\\+\tfrac{1}{2}\sum_{\mathbf{R},\mathbf{R}'}\mathbf{u}_{\mathbf{R}}\cdot\mathbf{\Phi}(\mathbf{R}-\mathbf{R}')\cdot\mathbf{u}_{\mathbf{R}'}-\sum_{\mathbf{R},\mathbf{R}'}\sigma_{\mathbf{R}}\mathbf{F}(\mathbf{R}-\mathbf{R}')\cdot\mathbf{u}_{\mathbf{R}'}+\mathcal{O}(\Delta V^3)\,,\end{aligned} \tag{5}$$

where $K \equiv \int \Delta v(\mathbf{r})n(\mathbf{r})d\mathbf{r}$ is a constant which does not contribute to the formation energy,

$$J(\mathbf{R}-\mathbf{R}')\equiv\int \Delta v(\mathbf{r}-\mathbf{R})\Delta n_v(\mathbf{r}-\mathbf{R}')d\mathbf{r}\,,$$

Δn_v is the electron charge linearly induced by Δv,

$$\mathbf{F}(\mathbf{R}-\mathbf{R}')\equiv-\int \Delta n_v(\mathbf{r}-\mathbf{R})\frac{\partial v}{\partial \mathbf{R}'}(\mathbf{r}-\mathbf{R}')d\mathbf{r}$$

is the force linearly induced on the virtual ion at site $\mathbf{R}'$ by the perturbation $\Delta v(\mathbf{r}-\mathbf{R})$ located at $\mathbf{R}$, and $\mathbf{\Phi}(\mathbf{R}-\mathbf{R}')$ is the matrix of the vibrational interatomic force constants of the virtual crystal.[4] Ion displacements are not independent variables: For any given ionic configuration $\{\sigma_{\mathbf{R}}\}$, their equilibrium values are those which minimize the quadratic form, Eq. (5). The minimum defines the *configurational energy* of the alloy, which is the sum of the chemical plus relaxation contributions to the formation energy, Eqs. (2) and (3):

$$\Delta E_{\mathrm{config}}\equiv\Delta E_{\mathrm{chem}}+\Delta E_{\mathrm{relax}}=\frac{1}{2}\sum_{\mathbf{R},\mathbf{R}'}\tilde{J}(\mathbf{R}-\mathbf{R}')\sigma_{\mathbf{R}}\sigma_{\mathbf{R}'}-\frac{N}{2}\sum_{R}J(\mathbf{R})\,, \tag{6}$$

where

$$\tilde{J}(\mathbf{R}-\mathbf{R}')=J(\mathbf{R}-\mathbf{R}')-\sum_{\mathbf{R}'',\mathbf{R}'''}\mathbf{F}(\mathbf{R}-\mathbf{R}'')\cdot\mathbf{\Phi}^{-1}(\mathbf{R}''-\mathbf{R}''')\cdot\mathbf{F}(\mathbf{R}'-\mathbf{R}''')$$

are renormalized interaction constants, and N is the number of atoms in the alloy. Equation (6) clearly displays the isomorphism between the alloy problem and a lattice gas with two-body—generally long-range—interactions, when third- and higher-order terms in perturbation theory are disregarded. In the following, we show that—for $\mathrm{Si}_x\mathrm{Ge}_{1-x}$—the second-order expansion given by Eq. (6) provides a very accurate description of the relevant energy differences.

All the necessary quantities—J, $\mathbf{F}$, and $\mathbf{\Phi}$—can be efficiently calculated using the Green's-function LRT method of Ref. 5, along lines similar to those exposed in Ref. 4(b). Calculations have been performed using norm-conserving pseudopotentials, basis sets of plane waves up to a kinetic-energy cutoff of 12 Ry, and six special points for Brillouin-zone integrations. Real-space interactions have been calculated using reciprocal-space and Fourier-transform techniques, as explained in Ref. 4(b), and exploiting crystal symmetry to reduce the number of independent interactions. Our reciprocal-space grid is such that it allows the calculation of J, $\mathbf{F}$, and $\mathbf{\Phi}$ in real space up to the 22nd complete shell of neighbors. Other technical details are the same as in Ref. 4(b).

In Table I we compare the chemical and relaxation contributions to the formation energies of several ordered structures of $\mathrm{Si}_x\mathrm{Ge}_{1-x}$, as obtained by the present approach and by accurate DFT self-consistent-field (SCF) calculations. Inspection of the table shows that the typical accuracy achievable by the present approach is of the order of (often better than) 5%, thus giving confidence in its predictive power.

In Fig. 1 we display the calculated interaction con-

TABLE I. Comparison between the configurational energies [Eq. (6)] of several superlattice structures, calculated by linear-response theory (LRT) and full self-consistent-field (SCF) calculation, both neglecting (unrelaxed) and including (relaxed) lattice relaxation (in meV/atom). The $n+m$ notation indicates n Si and m Ge layers; ZB stands for zinc blende. For [111] superlattices, the RH1 and RH2 labels refer to Si-Ge-Ge-Si and Si-Si-Ge-Ge stacking, respectively. All calculations are performed at the lattice constant given by Vegard's law for $x=\frac{1}{2}$.

	Unrelaxed		Relaxed	
Structure	LRT	SCF	LRT	SCF
ZB	−6.4	−6.5	−6.4	−6.5
$[001]_{2+2}$	−4.6	−4.6	−9.4	−9.7
$[001]_{3+1}$	−3.9	−3.9	−6.3	−6.4
$[001]_{1+3}$	−3.9	−3.9	−6.3	−6.5
$[001]_{3+3}$	−3.1	−3.2	−9.2	−9.5
$[111]_{2+2}^{\mathrm{RH1}}$	−5.9	−5.7	−9.9	−10.0
$[111]_{2+2}^{\mathrm{RH2}}$	−2.5	−2.5	−6.1	−6.3
$[111]_{3+3}$	−2.9	−3.0	−7.6	−7.9
$[110]_{2+2}$	−2.7	−2.7	−10.4	−10.7
$[110]_{3+1}$	−2.5	−2.5	−7.5	−7.8
$[110]_{1+3}$	−2.5	−2.5	−7.5	−7.9

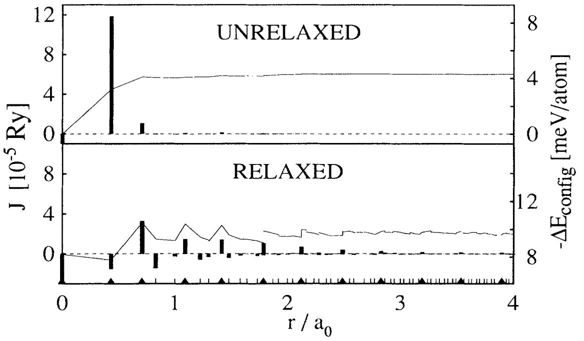

FIG. 1. Atomic interaction constants (thick vertical bars) calculated neglecting ("unrelaxed") and including ("relaxed") lattice relaxation, as functions of the interatomic separation r. "On-site" interactions $r=0$ are not reported because they would be off scale. Thin vertical bars on the horizontal axis indicate shells of neighbors. Shells lying on the same bond chain as the atom at the origin are indicated by a solid triangle. The solid lines indicate the formation energy of the random alloy in the regular-solution approximation, obtained by truncating the interaction at a given shell of neighbors.

stants as functions of the interatomic distance, calculated at the lattice parameter given by Vegard's law for $x=\frac{1}{2}$. Neglecting lattice relaxation (upper panel), the interactions are quite short range, and practically vanish beyond the third shell of neighbors. Lattice relaxation makes the interactions propagate rather far along the bond chains (lower panel).[6] The solid lines indicate the value of configurational energy of the random alloy, Eq. (6), calculated using the regular-solution approximation and truncating the interaction constants at different shells of neighbors. In the unrelaxed case the convergence is very rapid and a few interaction constants suffice. When relaxation is included the convergence is slow and drops are observed in correspondence with shells containing atoms belonging to the same bond chain as the atom at the origin. This indicates that a larger number of interaction constants have to be considered.

Let us compare the present approach to the RIM method of Ref. 2. Contrary to the present approach, RIM is not bound to systems whose chemical disorder is weak: In fact, many-body interactions can be extracted in a similar way as two-body ones, whereas in our approach the calculation of many-body interactions is possible in principle but not very practical. On the other hand, the actual application of the RIM rests on the possibility of extracting interaction constants from calculations made for small supercells. If the range of the interactions is larger than the size of the supercells one can deal with, short-range interactions will be affected by the neglect of long-range ones. We conclude that in these cases RIM could only provide an approximate scheme even in the limit of weak chemical disorder, whereas our scheme (which is based on perturbation theory and is not limited by the size of any supercell) is exact in that limit. Assessing the importance of the differences between the two methods—as applied to semiconductor alloys—requires in our opinion further research.

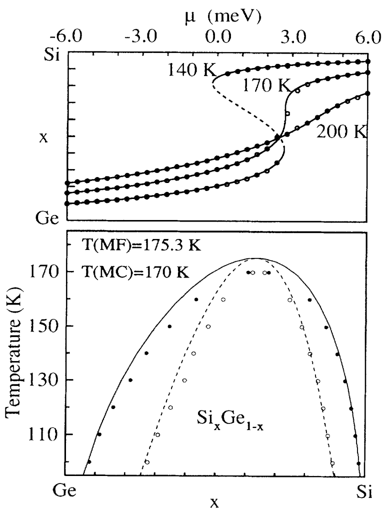

FIG. 2. Top panel: Average Si concentration of the alloy as a function of the chemical potential, for three different temperatures. The lines are obtained by a fitting procedure, as described in the text. The dashed portion of the line at 140 K corresponds to the instability region inside the spinoidal line. Bottom panel: Phase diagram of SiGe alloys. Circles: Monte Carlo predictions for the miscibility gap (solid circles) and spinoidal (open circles) lines. Lines: Mean-field predictions for the same lines (solid and dashed lines, respectively).

We now illustrate how the present method can be used to calculate thermodynamic properties by Monte Carlo (MC) simulations. We have performed constant-pressure ($P=0$), constant-chemical-potential MC simulations on a system of 1024 atoms: To this end, interaction constants for an arbitrary volume are obtained by quadratic interpolation of the values calculated for three different volumes (near the equilibrium volumes of pure Si, pure Ge, and $Si_{0.5}Ge_{0.5}$, as given by Vegard's law). In the top panel of Fig. 2 we display the average concentration x as a function of the chemical potential μ,[7] obtained for three different temperatures (above, below, and at the critical temperature T_c). The statistical errors are estimated to be smaller than the displayed circles. Above T_c, the concentration is a continuous function of the chemical potential, thus indicating complete miscibility for any concentration. As the temperature decreases below T_c, a discontinuity appears which signals the opening of a miscibility gap. The free energies of the Ge- and Si-rich phases are obtained by integration: To this end, the dependence of the chemical potential upon concentration is fitted by the function

$$\mu(x)=kT\ln\left(\frac{x}{1-x}\right)+\frac{dP(x)}{dx},$$

where $P(x)$ is a fourth-order polynomial which vanishes at $x=1$ and 0, so that the correct high- and low-

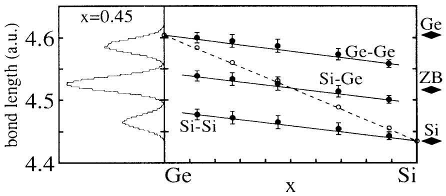

FIG. 3. Left panel: Bond-length distribution in $Si_{0.45}Ge_{0.55}$ alloys, measured by MC simulation at $T=300$ K. Right panel: Dependence of maxima of the peaks upon Si concentration (solid circles, the error bars indicate the width of the peaks); dependence upon composition of the average bond length, as obtained from the alloy lattice parameter (open circles). The solid and dashed lines are intended as guides for the eyes. The diamonds on the right indicate the equilibrium bond lengths of pure Si and Ge and of zinc-blende SiGe.

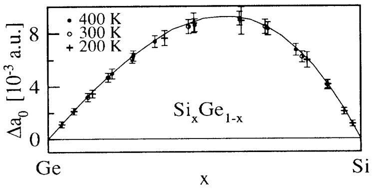

FIG. 4. Deviations of the alloy lattice parameter from linearity with respect to concentration (Vegard's law). All the data taken in the temperature range between 200 and 400 K coincide with those predicted by the regular-solution approximation, within statistical errors.

concentration limits are enforced. The miscibility gap is found corresponding to the values of the chemical potential where the two phases have the same free energy (lower panel, solid circles), whereas the maximum and minimum of $\mu(x)$ appearing below T_c correspond to the spinodal line (lower panel, open circles). The line of the miscibility gap and the spinodal line obtained by the mean-field (MF) approximation are also displayed, by the solid and dashed lines, respectively. The value of T_c estimated by MC simulation is ≈ 170 K, whereas the MF approximation gives 175.3 K. The two results are quite close—although the MF approximation overestimates T_c as expected—as the thermodynamics of the system is dominated by the (configuration-independent) elastic contribution to the formation energy. Our results are at variance with previous cluster-expansion calculations,[8] but they agree well with recent MC simulations employing semiempirical interatomic potentials.[9]

MC simulations allow us to calculate the bond-length distribution in the alloy as a function of the molar composition. In Fig. 3 we display our results obtained at $T=300$ K. The histogram in the left panel displays the bond-length distribution corresponding to an average composition $x=0.45$, and shows three distinct peaks whose maxima are close to—but do not coincide with—the equilibrium bond lengths of pure Si, pure Ge, and zinc-blende SiGe (reported on the right of the figure). In the right panel, we summarize our results for different concentrations. Solid circles indicate the maxima of the peaks, error bars their widths, and open circles indicate the average bond length, as obtained by the lattice constant of the alloy. These data do not depend on temperature for any temperature above T_c, within our statistical errors, and they indicate that Vegard's law is followed very closely. Deviations of the average lattice parameters from Vegard's law—as obtained for different temperatures in the range of 200–400 K—are displayed on a magnified scale in Fig. 4, along with the predictions of the regular-solution approximation (solid line). All the data coincide with the predictions of this approximation, thus confirming that Si_xGe_{1-x} is a model random alloy at all temperatures in this range and, *a fortiori,* at higher temperatures. These results clearly indicate that the mechanisms responsible for the spontaneous ordering observed in epitaxially grown Si_xGe_{1-x} alloys[10] should not be searched for in bulk thermodynamics. Rather, they could be related to kinetic effects[11] and/or to surface thermodynamics.

This work has been cosponsored by the Italian Consiglio Nazionale delle Ricerche under Grant No. 89.00006.69, by the Swiss National Science Foundation under Grant No. 20-5446.87, and by the European Research Office of the U.S. Army under Grant No. DAJA 45-89-C-0025.

---

[1] See, e.g., D. de Fontaine, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1979), Vol. 34, p. 73.

[2] L. G. Ferreira, S-H. Wei, and A. Zunger, Phys. Rev. B **40**, 3197 (1989); S-H. Wei, L. G. Ferreira, and A. Zunger, Phys. Rev. B **41**, 8240 (1990).

[3] S. Baroni, R. Resta, B. Baldereschi, and M. Peressi, in *Spectroscopy of Semiconductor Microstructures,* edited by G. Fasol, A. Fasolino, and P. Lugli, NATO Advanced Study Institute Ser. B, Vol. 106 (Plenum, New York, 1989), p. 251; M. Peressi, S. Baroni, A. Baldereschi, and R. Resta, Phys. Rev. B **41**, 12 106 (1990).

[4] (a) S. Baroni, S. de Gironcoli, and P. Giannozzi, Phys. Rev. Lett. **65**, 84 (1990); (b) P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni (to be published).

[5] S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987).

[6] The same is true for vibrational interatomic force constants, as discussed in Ref. 4.

[7] The "chemical potential" of the auxiliary lattice gas is indeed the difference between the Si and Ge chemical potentials.

[8] A. Qteish and R. Resta, Phys. Rev. B **37**, 6983 (1988).

[9] P. C. Kelires and J. Tersoff, Phys. Rev. Lett. **63**, 1164 (1989).

[10] A. Ourmazd and J. C. Bean, Phys. Rev. Lett. **55**, 765 (1985); D. J. Lockwood, K. Rajan, E. W. Fenton, J.-M. Baribeau, and M. W. Denhoff, Solid State Commun. **61**, 465 (1987).

[11] F. K. LeGoues, V. P. Kesan, S. S. Iyer, J. Tersoff, and R. Tromp, Phys. Rev. Lett. **64**, 2038 (1990).