RAPID COMMUNICATIONS

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Ordering and decomposition in semiconductor alloys

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The stability of ordered semiconductor alloys has been studied, using total energy pseudopotential calculations. The ordered alloys are found to be stabilized with respect to

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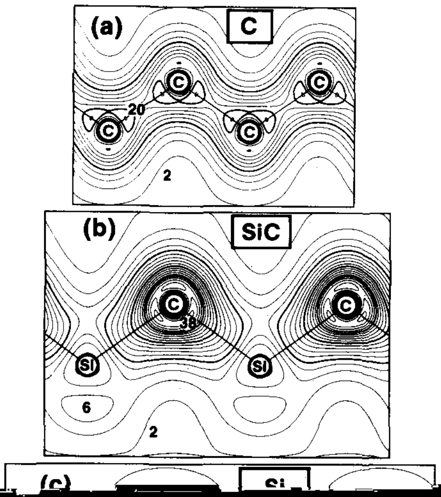
formed within the pseudopotential local density formalism. Our calculation is based on a first-principles total energy minimization within the nonlocal pseudopotential representation of the local density formalism.[12] It uses an extensive plane wave basis set, including all plane waves with kinetic energies less than of 50 Ry for C and SiC, and 24 Ry for Si, Ge, and SiGe. For complex unit cells we use a cutoff of 18 or 12 Ry. Ten special **k** points are used for Brillouin zone integration for diamond or zincblende phases, and the **k** points obtained by folding two special **k** points of the fcc Brillouin zone are used in the other cases. The only empirical inputs are the atomic numbers and the crystal space groups.

For ordered (O) phases of alloys we first enumerate the tetrahedral adamantine space groups which are likely to occur using the Landau–Lifshitz theory.[13,14] We then calculate their total energy, including thereby both strain and chemical effects on the same basis, by performing a minimization of the total energy with respect to structural parameters.

The choice of ordered structures involves the use of

single kind of atom (e.g., the C atom in $A_{1-x}B_xC$) and order the other sublattice as if it was a simple fcc structure. Figure 1 shows four (out of eight) of the structures obtained in this way, with information about their structural symmetries and diffraction patterns. These sets contain the three known structures of ternary semiconductors and one of an existing artificial structure (the CuAu-I structure[3]). In the case of the $A_{1-x}B_x$ semiconductor alloys (e.g., Si_xGe_{1-x}), the LL theory yields 32 structures with each sublattice occupied by one of the eight fcc patterns (enumerated by Khachaturyan[14]) plus the simple fcc lattice itself. According to Khachaturyan[14] both sublattices should have the same symmetry (e.g., the first three structures in Fig. 2, which include the observed CuPt ordering[4]), but we have also considered some structures where the symmetry of one sublattice is a subgroup of the symmetry of the other sublattice (e.g., the last two structures of Fig. 2). Notice that the two sublattices need not have the same composition and different structures can be built from the same pair of sublattices by changing their relative



tice constants, hence additional macroscopic strain), we expect to find at lower temperatures *ordering in a metastable phase*. Therefore, at low temperatures one can expect to find either truly stable ordered phases ($\Delta H^{(O)} < 0$), or metastably ordered phases ($0 < \Delta H^{(O)} < \Delta H^{(D)}$). According to our calculations of the enthalpy of ordered $\mathrm{Si}_n\mathrm{Ge}_m$ alloys, these phases should be metastable in bulk form, which is in agreement with the experimental observations[4] of ordering in $\mathrm{Si}_x\mathrm{Ge}_{1-x}$: the strongest superlattice diffraction peaks were observed after half an hour of annealing at 450 °C, but if the annealing was prolonged the order *decreased*, an effect attributed[4] to the diffusion of Ge from the alloy into the Si substrate. (Epitaxial SiGe/Si: is, however, predicted[2] to be stable.) A consistent picture of the metas-

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