$Si_xGe_{(1-x)}$ simulations with hybrid exchange-correlation functionals

Jacopo Masnaghetti[a,b], Guido Fratesi[a], Alberto Debernardi[b,*]

[a] *Dipartimento di Fisica "Aldo Pontremoli", Università degli Studi di Milano, Via G. Celoria 16, Milano, 20133, Italy*
[b] *IMM-CNR, Via Camillo Olivetti 2, Agrate Brianza, 20864, Italy*

Silicon-germanium random alloys have many applications in microelectronics, including photovoltaic and infra-red sensors. Work in these fields requires a good knowledge of the electronic bands structure, thus ab-initio simulations can be a useful tool for the design and production of effective devices. Experimental evidences show that the band gap in $Si_xGe_{(1-x)}$ random alloy, where x represents the silicon concentration, varies as a function of x following two distinct trends; for $0.0 < x < 0.15$, the conduction band minimum is positioned along the <1 1 1> direction at the edge of the Brillouin zone, like in germanium, and its value varies linearly with x, whereas for $x > 0.15$ the conduction band minimum is positioned along the <1 0 0> direction, like it happens in silicon, and the band gap dependence is parabolic [1]. However, standard GGA-DFT calculations severely underestimate the band energy gap in silicon and makes germanium a semimetal, instead of the correct indirect gap semiconductor. To solve this problem, this contribution proposes and implements a variation of the technique presented in Darmody et al. 2015 [2], that uses a combination of lattice compression and hybrid PBE0 exchange-correlation functional.
We fit the energy gaps of both bulk materials to a second degree polynomial function in which the mixing parameter of the hybrid functional and the lattice pressure are independent variables; we then use these fitted functions to find the values of the two variables that makes the simulated energy gaps the closest to the experimental evidence. Since we are trying to simulate the correct gaps for two different materials at the same time, some level of compromise must be accepted. We found the best parameter to recreate the values of the energy gaps within 1% of the experimental values at the cost, however, of having the direct band gap of germanium being only 0.01 eV larger than the indirect one, instead of the correct 0.15 eV. Then, we simulate the evolution of the energy gap in $Si_xGe_{(1-x)}$ using the best-fit values of pressure and mixing parameter with 8, 16 and 32-atom-supercells in QUANTUM ESPRESSO [3]. The random structure of the alloy is mimicked using the Special Quasi Random Structure (SQS) approach [4], implemented through the mcsqs software of the Alloy-Theoretic Automated Toolkit (ATAT) [5]. Our calculations show that using 8-atom-supercells produces gaps in good agreement with the experimental data for $0.0 < x < 0.15$, but not for $0.15 < x < 1.0$, nor it correctly models the change in position of the band gap minimum. On the other hand, when 16-atom-supercells are used, the agreement is bad in the linear region, but it improves for $x > 0.3$, while again failing in predicting the transition of the conduction band minimum. The 64-atoms-supercells provided the best results, with the gaps showing linear and quadratic evolution in the correct intervals (Fig.1) and correctly predicting the position of the conduction band minimum for all but two (x=0.1875 and x=0.25) of the simulated compositions.

References:

1. J. Weber, M.I. Alonso, Phys. Rev. B 40, 5683—5693 (1989)
2. C. Darmody, D.P. Ettisserry, N. Dhar, 2015 International Conference on Simulation of Semiconductor Processes and Devices, (IEEE, 2015,Washington DC) 329-332.
3. P Giannozzi et al 2017 J. Phys.:Condens. Matter 29 465901
4. A. Zunger, S. H. Wei, L. G. Ferreira, J. E. Bernard, Phys. Rev. Lett. 65, 353-356 (1990)
5. A. van de Walle, P. Tiwary, M. de Jong, D.L. Olmsted, M. Asta, A. Dick, D. Shin, Y. Wang, L.Q. Chen, Z.-K. Liu, Calphad 42, 13-18 (2013)

**corresponding author e-mail: alberto.debernardi@mdm.imm.cnr.it*

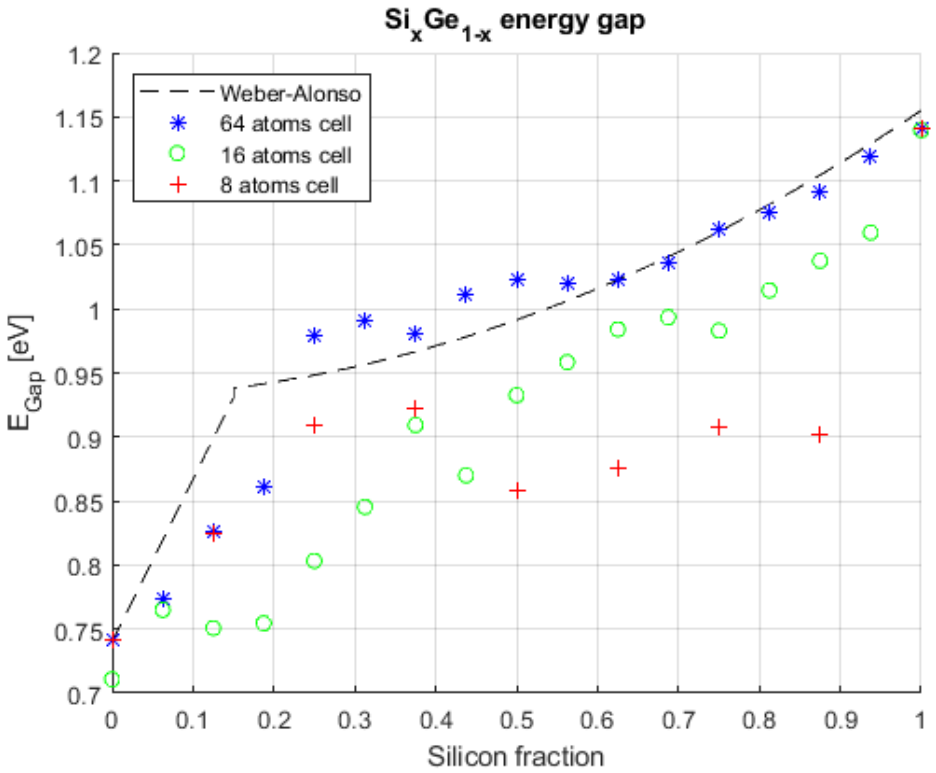

Fig 1: energy gap as a function of x, the dotted line represents the experimental evidence from [5]

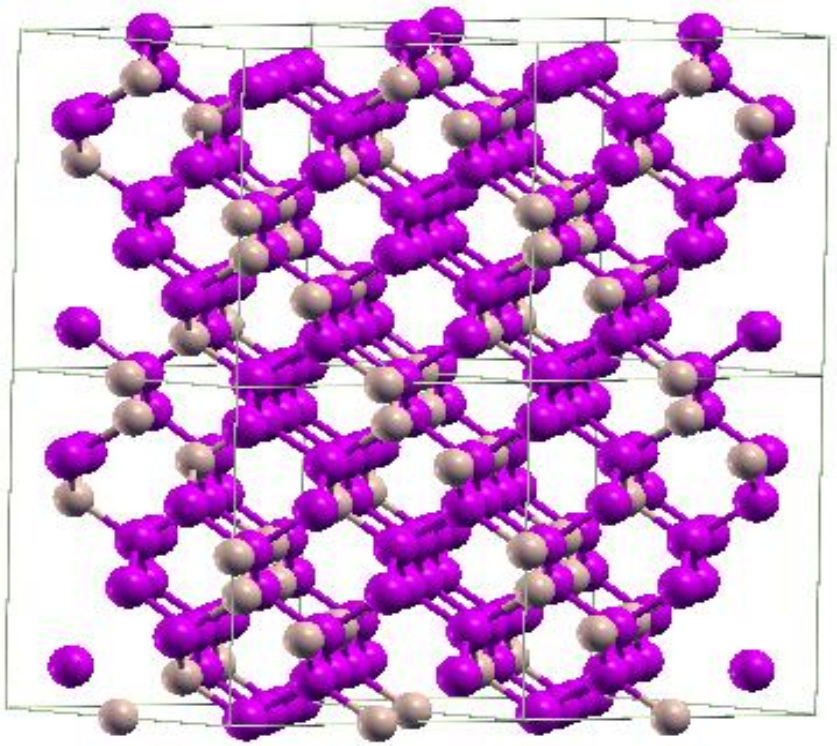

Fig 2: 16-atom-supercells with x=0.25, 4 supercells are shown in total