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Structure of Sn$_{1-x}$Ge$_x$ random alloys as obtained from the coherent potential approximation

J. J. Pulikkotil, A. Chroneos, and U. Schwingenschlögl

\textit{1}PSE Division, KAUST, Thuwal 23955-6900, Saudi Arabia
\textit{2}Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB2 3QZ, United Kingdom

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The structure of the Sn$_{1-x}$Ge$_x$ random alloys is studied using density functional theory and the coherent potential approximation. We report on the deviation of the Sn$_{1-x}$Ge$_x$ alloys from Vegard’s law, addressing their full compositional range. The findings are compared to the related Si$_{1-x}$Ge$_x$ alloys and to experimental results. Interestingly, the deviation from Vegard’s law is quantitatively and qualitatively different between the Sn$_{1-x}$Ge$_x$ and Si$_{1-x}$Ge$_x$ alloys. An almost linear dependence of the bulk modulus as a function of composition is found for Si$_{1-x}$Ge$_x$, whereas for Sn$_{1-x}$Ge$_x$ the dependence is strongly nonlinear. © 2011 American Institute of Physics. [doi:10.1063/1.3618671]

Group IV semiconductor alloys and, in particular, Si$_{1-x}$Ge$_x$ are important materials for microelectronic and optoelectronic applications.\textsuperscript{1–5} Early studies demonstrated that Si$_{1-x}$Ge$_x$ alloys are effectively random alloys.\textsuperscript{6–8} Although Si$_{1-x}$Ge$_x$ alloys have been investigated very thoroughly for a number of years, Sn containing alloys have received less attention.\textsuperscript{1–11} Sn$_{1-x}$Ge$_x$ alloys are technologically interesting as they can have direct energy gaps tunable from 0 to 0.55 eV over their full compositional range. The aim of the present paper is to establish (by advanced \textit{ab-initio} techniques) insight into the lattice constant, the bulk modulus, and the pressure derivative of the bulk modulus of Sn$_{1-x}$Ge$_x$ alloys over their full compositional range. For comparison, the same computational methodology is employed to Si$_{1-x}$Ge$_x$.

The ground state properties are calculated by the Korringa-Kohn-Rostoker (KKR) method formulated in the atomic sphere approximation (ASA).\textsuperscript{24} The potential of the disordered material is modeled in the coherent potential approximation (CPA). For improving the alloy energetics, the ASA is corrected by the muffin-tin correction as well as the multipole moment correction to the Madelung potential and energy. These two corrections significantly improve the accuracy of the total energy by taking into account the non-spherical part of the polarization effects.\textsuperscript{25,26} In order to fill the volume, we have used empty spheres. The atoms are placed at the 8(a) Wyckoff positions (1/8,1/8,1/8) of the \textit{Fd}$_3$\textit{m} cubic system, while empty spheres are introduced at the 8(b) Wyckoff positions (3/8,3/8,3/8). In this way, the volume overlap is 14%, which is well within the limits of the approximation.

The partial waves in the KKR-ASA calculations are expanded up to $l_{\text{max}} = 3$ inside the muffin-tin spheres even though the multipole moments of the electron density are determined up to $l_{\text{max}} = 6$. Exchange-correlation effects are treated in the generalized gradient approximation (GGA),\textsuperscript{27} which leads to an overestimation of properties such as band gaps and formation energies of defects.\textsuperscript{28} Nevertheless, deviations from Vegard’s law or relative defect energies can be predicted in excellent agreement with the experiment.\textsuperscript{29,30} In our calculations, the core states are recalculated after each iteration. Moreover, the overlap volume resulting from the blow-up of the atomic spheres is less than 12%, which is within the accuracy of the approximation. In the self-consistency cycle, a Monkhorst-Pack\textsuperscript{31} $k$-mesh of grid size 12 x 12 x 12 is applied, which corresponds to 182 $k$-points in the irreducible part of the Brillouin zone. Convergence of the charge density is achieved such that the root mean square of moments of the occupied partial density of states (DOS) becomes smaller than $10^{-5}$.\textsuperscript{a,b}
To study the effects of atomic relaxation in the Sn$_{1-x}$Ge$_x$ and Si$_{1-x}$Ge$_x$ alloys, we use the force minimization technique as implemented in the WIEN2k package.\cite{bib:03}

To model disorder, we make use of the SQS approach, the efficacy of which has been demonstrated previously.\cite{bib:33} SQS cells mimic the most relevant near neighbor pair and multisite correlation functions of the alloy. We apply the 64 atom supercell that has been reported in a previous study\cite{bib:29} and has shown to be appropriate for SiGe and SnGe alloys.\cite{bib:11, bib:23}

The local chemical environments of the atoms are not altered, as force minimization here refers to relaxation of the ionic coordinates only. Figures 1 and 2 show (a) the lattice constant, (b) the deviation from Vegard’s law, (c) the bulk modulus, and (d) the pressure derivative of the bulk modulus for the Si$_{1-x}$Ge$_x$ and Sn$_{1-x}$Ge$_x$ alloys, respectively.

For Si$_{1-x}$Ge$_x$ alloys, there are detailed reports on the deviation from linearity. It is established that our calculations are in excellent agreement with these experimental and theoretical results, which constitute a negative deviation from Vegard’s law, see Fig. 1 (Refs. 1 and 37). The negative deviation implies that the Si-Ge chemical bonding is stronger than the Si-Si and Si-Ge bonding. Therefore, the deviation from Vegard’s law is the highest for Si$_{0.5}$Ge$_{0.5}$ where the concentration of Si-Ge bonds is maximized (Fig. 1). Conversely, for the Sn$_{1-x}$Ge$_x$ alloys we obtain a positive deviation from Vegard’s law, see Fig. 2. This agrees with the experiments of Chizmeshya et al.,\cite{bib:10} which, however, are limited to Sn-rich Sn$_{1-x}$Ge$_x$ alloys and show significant effects of scattering. The present results are also consistent with previous DFT-SQS calculations,\cite{bib:23} which again have only considered Sn-rich Sn$_{1-x}$Ge$_x$.

In a strict theoretical sense, CPA and SQS results are similar. However, since forces are covered by the supercell SQS calculations but not by the CPA, we address the equiatomic alloys. We find that for equiatomic SiGe composition, the forces are significantly smaller than in the SnGe case. To find a stable equilibrium structure, we thus perform force minimization. Studying in more detail the compound Si$_{0.5}$Ge$_{0.5}$ we observe that on average the (shorter) Si-Si bonds are compressed by 0.044 Å and that the Ge-Ge bonds are elongated by 0.028 Å, whereas the modifications of the Si-Ge bonds are negligible. For Sn$_{0.5}$Ge$_{0.5}$ our results show that on average the (now shorter) Ge-Ge bonds are compressed by 0.144 Å and the Sn-Sn bonds expand by 0.141 Å, while only a small modification of 0.01 Å affects the Sn-Ge bonds. Thus, the bonds of the bigger atoms elongate, whereas the bonds of the smaller atoms get compressed. It may be noted that the present approach is strictly valid for the periodic conditions of the supercell. The local chemical environments of the atoms are not altered, as force minimization here refers to relaxation of the ionic coordinates only.

Turning our attention to the variation of the bulk modulus (Figs. 1 and 2) as a function of the Ge content there are...
again big differences between the two materials. For Si$_1$-xGe$_x$, we find that the bulk modulus decreases almost linearly with increasing Ge content. Interestingly, however, for Sn$_1$-xGe$_x$ an increasing Sn content results in a quadratic dependence of the bulk modulus.

Considering the pressure derivative of the bulk modulus, we find an increase for Si$_1$-xGe$_x$ as the Ge content is increased. However, for Sn$_1$-xGe$_x$ there is an almost “inverse parabolic” behavior. In the Debye model, the pressure derivative of the bulk modulus contains information about the averaged lattice vibrations of the material by means of the Grüneisen parameters. Interestingly, the Grüneisen parameters of Ge and z-Sn (diamond structure) are comparable, while for Si and Ge they are considerably different.38–40 In a recent experimental study, Roucka et al.41 have determined a very similar behavior for the compositional dependence of the linear thermal expansivities of the Si$_1$-xGe$_x$ and Sn$_1$-xGe$_x$ alloys. Notably, the linear thermal expansivity α(T) and the bulk modulus B are linked to the Grüneisen parameters via the relation42

$$a(T) = (1/3B) \sum q_n^2 \varepsilon_n,$$

where $\varepsilon_n(q)$ is the Grüneisen parameter of the vibrational mode with wave vector $q$ and branch index $n$, and $c_{nq}$ is the mode’s contribution to the specific heat. Revisiting Roucka et al.41 as there is a volume dependence of the Grüneisen parameters (for Si and Ge refer to Refs. 43 and 44), the different deviations from Vegard’s law in Figs. 1 and 2 and the compression or elongation of the respective bonds in Si$_1$-xGe$_x$ and Sn$_1$-xGe$_x$ will affect these two alloys differently. The present results indicate that there is a strong nonlinear dependence of the bulk modulus in the case of the Sn$_1$-xGe$_x$ alloys, which will affect the linear expansivity.

Ab-initio calculations in conjunction with the CPA have been used to study the structural properties of the Sn$_1$-xGe$_x$ and Si$_1$-xGe$_x$ (for comparison) alloys. The entire compositional range has been addressed in order to establish a comprehensive picture. We observe that the deviation from Vegard’s law for Sn$_1$-xGe$_x$ is opposite in sign and different in magnitude as compared to the Si$_1$-xGe$_x$ alloys. The bulk modulus and its pressure derivative are strongly nonlinear for the Sn$_1$-xGe$_x$ alloys. These observations can explain the nonlinear compositional dependence of the linear thermal expansivity of the Sn$_1$-xGe$_x$ alloys (in contrast to the much more linear behavior exhibited by the Si$_1$-xGe$_x$ alloys).

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