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Thermodynamic properties of Si-Ge alloys

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A combined electronic-structure and statistical-mechanical approach has been used to calculate the thermodynamic properties of $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloys. Since the long-range ordered structures are found to be unstable, only the disordered alloys have been studied. The thermodynamic functions such as entropy, enthalpy, Gibbs free energy, and others are calculated as functions of temperature and concentration. The phase diagram is also calculated and the critical temperature is predicted to be around 360 K. The tendency to clustering is found to be very small which provides further support for the instability of ordered bulk Si-Ge structures. We have studied the effects of hydrostatic pressure on both the phase diagram and the thermodynamic functions. It has been found that by increasing the pressure the instability region shrinks and moves toward the Ge side, while the critical temperature increases.

I. INTRODUCTION

In spite of the technological importance of the semiconducting alloys the present understanding of their thermodynamic properties is far from satisfactory. Metallic alloys have been studied more, and several calculations of their thermodynamic properties, performed using a combined electronic-structure and statistical-mechanical approach, have appeared in the literature over the years.[1-4] Some work in the same spirit and concerning semiconducting alloys has appeared very recently;[5] state of the art electronic-structure calculations are able to provide very accurate energies, while they deal with both elastic and chemical contributions on the same footing.

Previously, only phenomenological approaches were undertaken. Balzarotti and co-workers[6] have studied the thermodynamic properties of some ternary semiconducting alloys, using elastic energies calculated by a valence field method[7] and chemical energies extracted from the experimental values of the interaction parameter. This approach gives a positive chemical contribution to the formation energies of the ordered structures, contrary to the present understanding. Other theoretical models[8-12] can be considered as incomplete. The most recent first-principles work of Mbaye, Ferreira, and Zunger has shown[3,5] that proper accounting for the chemical energy is essential and leads to new features in the phase diagram.

In a previous paper,[13] hereafter referred to as I, we have introduced a model for the local atomic structure of binary semiconducting alloys; in our model the basic unit is a five-site tetrahedron. Nine different ordered structures (each corresponding to different configuration of tetrahedra) have been studied using the density-functional theory[14,15] and norm-conserving pseudopotentials.[16] For the disordered materials, the energy of mixing and hence the interaction parameter have been calculated by assuming a completely random distribution of the atoms at the lattice sites (Bernoulli distribution of tetrahedra) which is temperature and system independent, and the linear variation of the lattice constant (Vegard's law).

Using the formation energies of the configurations calculated previously, we calculate in this work the probability distribution of tetrahedra, as functions of concentration (x) and temperature (T), in the framework of two different approximations. The first is the modified quasichemical approximation (sometimes referred to as the third-order quasichemical approximation[6] (QCA).[17] The second approximation we use is the cluster-variation method (CVM).[18,19] Since no ordered structure has been found to be stable at $T=0$ and increasing the temperature is not expected to stabilize any of them, we will study only the disordered $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloys. Due to our structural model which distinguishes between the sites of the two sublattices, only constrained CVM calculations can be performed, while QCA calculations do not present any problem. The enthalpy, entropy, free energy, interaction parameter, and the tendency to clustering as functions of x and T are calculated. The phase diagram has been calculated and the critical temperature is predicted to be around 360 K at zero pressure. We have performed a similar study under hydrostatic pressure: our main findings are that the thermodynamic quantities and the phase diagram are strongly affected by pressure.

The rest of this work is organized as follows. In Sec. II we describe briefly the main features of the structural model. In Sec. III we give the basic equations and definitions of the thermodynamic functions. In Sec. IV we report and discuss the results obtained at zero pressure. In Sec. V we discuss the effects of applying a hydrostatic pressure on the thermodynamic properties. Finally, Sec. VI contains the main conclusions.

II. THE MODEL

Recently we have proposed in I a model for the atomic microscopic structure of binary semiconducting alloys in the spirit of a previous model for ternary alloys,[6,12] and we applied it to calculate (at $T=0$ and $P=0$) the micro-

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scopic atomic structure and the energy of mixing for Si_xGe_{1-x} alloys. The calculations are performed within the framework of density-functional theory[14] using the local-density approximation[15] and norm-conserving pseudopotentials.[16] Here we will discuss briefly the basic features of our model.

The key assumption of our model implies that all of the possible local structures can be realized in coherent periodic structures. We assume that one of the sublattices (arbitrarily chosen) is undistorted, while the other is allowed to relax. In this way we perform only constrained energy minimization; our building unit is a five-site tetrahedron (an atom plus its four first-nearest neighbors), whose vertices belong to the undistorted fcc sublattice; the inside atom is allowed to relax. Because the direction of the relaxation is determined by symmetry, the distortion of the inside atom can be determined by a single scalar parameter; more details and figures are given in I. Since the atom inside the tetrahedra can be either A or B type (for A_xB_{1-x} alloys), there are ten local configurations. In the present work we denote them as A_n and B_n, where A (B) refers to the inside atom and $n=0,1,2,3,4$ is the number of A atoms at the vertices. The present notations are *not* the same as in I, the reason for the change being the simplification we get in the expression for the thermodynamic functions. The simplest ordered structures which realize the local configurations are found to have very few atoms per unit cell (up to eight). Considering the five-site tetrahedron as a basic unit makes this model analogous to the central-atom model of Lupis and Elliot[20] or the surrounding-atom model of Mathieu and co-workers.[21] Very recently a similar model has been introduced to calculate the frequency-dependent dielectric function of Si_xC_{1-x} alloys.[22]

Our approximation of assuming one of the two sublattices as undistorted (despite the physical equivalence of the two sublattices in binary alloys) amounts to study relaxation at the level of the first neighbors only. This is indeed a very good approximation, as is discussed in the following. The energy of mixing can be unambiguously split into two parts (see, e.g., Ref. 5): (i) the volume-deformation contribution, which is the elastic energy needed to stretch and expand the lattice constants of the constituent materials to match that of the alloy, and is model independent; (ii) the chemical contribution, which is the remaining term, due to both charge transfer and relaxation of the bond angles and bond lengths. In I we have calculated the charge transfer, which is pretty small and independent of the local environment, while the local geometrical relaxation gives very tiny contributions. The first-principles theory deals with all the terms on the same ground; our approximation, roughly speaking, accounts completely for the elastic term and for the charge-transfer part of the chemical term, while the remaining local relaxation is partly accounted for. The numerical accuracy of our first-principle calculations, in connection with the reliability of the results, has been discussed thoroughly in I. Our results compare favorably with the experiment,[23] while the virtual-crystal approximation gives energies of mixing which are wrong by one order of magnitude.

III. BASIC DEFINITIONS AND EQUATIONS

In the determination of the thermodynamic properties of alloys the most difficult part is the calculation of the configurational entropy, which by definition is related to the number of possible ways (g) of distributing the atoms of the constituent materials at the lattice sites. The calculation of this quantity is a very difficult task and exact solutions are not possible; to proceed one has to make some approximations. In our model described in Sec. II, the basic unit or cluster is a five-site tetrahedron; using this as a basic cluster approximate expression for the entropy can be obtained by adopting a modified QCA of Guggenheim[17] or using the CVM of Kikuchi.[18,19]

Within the modified QCA it is assumed[17,24] that g is proportional to the number of arrangements corresponding to a random distribution of five-site tetrahedra (pairs in the case of simple QCA), where the proportionality constant can be obtained from the limit of complete randomness, i.e.,

$$g=\frac{N!}{\prod_i N_i!}\,\frac{\prod_{i,j,k,l,m}(N_i z^{(B)}_{ijklm})!}{\prod_{i,j,k,l,m}(N_i z_{ijklm})!}\,, \tag{1}$$

where $i,j,k,l,m=1$ or 2, 1 (2) referring to A (B) atoms; z_{ijklm} is the concentration of the *ijklm* tetrahedra with inside atom i; the superscript B in the above expression refers to the Bernoulli distribution. In Eq. (1) equivalent configurations are counted separately. The corresponding entropy is

$$S^{(\mathrm{QCA})}=-k_B\left[\sum_i x_i\ln x_i+\sum_{i,j,k,l,m}(z^{(B)}_{ijklm}\ln z^{(B)}_{ijklm}-z_{ijklm}\ln z_{ijklm})\right]\,, \tag{2}$$

which at a given concentration is an explicit function of z_{ijklm}.

In order to implement a CVM approach to our material one has to consider also all of the possible subclusters of the five-site tetrahedron. Those giving nonvanishing contributions are, in increasing order of complexity: points, first and second nearest-neighbor pairs, and tetrahedra surrounding an interstitial site in zinc-blende structure. We call the concentration of each of these clusters x_i, $y^{(1)}_{i,j}$, $y^{(2)}_{i,j}$, and w_{ijkl}, respectively. In this notation the CVM expression is given, following the lines of Ref. 25, as

$$S^{(\mathrm{CVM})}=-k_B\left[8\sum_i x_i\ln x_i+\sum_{i,j,k,l,m}z_{ijklm}\ln z_{ijklm}+\sum_{i,j,k,l}w_{ijkl}\ln w_{ijkl}-2\sum_{i,j}y^{(1)}_{ij}\ln y^{(1)}_{ij}-6\sum_{i,j}y^{(2)}_{ij}\ln y^{(2)}_{ij}\right]\,, \tag{3}$$

where x_i and z_{ijklm} have the same meaning as in Eq. (2). Both the QCA and CVM are members of a hierarchy of cluster-variation approximation; the explicit appearance in the latter of the concentrations of some of the subclusters takes, so to speak, care of the cooperative nature of the problem. Therefore it is a common belief among the workers in the field[18,26,27] that the CVM is in general more accurate than the QCA. It is worth mentioning, however, that a rigorous analysis by Schlijper[28] has shown that some supplementary assumption is needed to ensure the convergence to the exact value at the thermodynamic limit, upon increasing the hierarchy of the CVM approximations.

The tetrahedra concentrations and the entropy as functions of x and T can be found by minimizing with respect to the independent variables z the Gibbs free energy of mixing

$$G=\Delta H-TS\ , \tag{4}$$

where ΔH is the enthalpy of mixing defined by

$$\Delta H(x,T)=\sum_{i,j,k,l,m} z_{ijklm}(x,T)\Delta E_{ijklm}(a(x))\ , \tag{5}$$

under the constraint

$$\sum_{i,j,k,l,m}(n_{ijklm}-5x)z_{ijklm}=0\ , \tag{6}$$

where n_{ijklm} is the number of A atoms in the $ijklm$ cluster, which takes into account both the fixed concentration and the normalization condition (the sum of the variables z is equal to one). So, the free energy to be minimized is

$$G(x,T)=\sum_{i,j,k,l,m} z_{ijklm}(x,T)\Delta E_{ijklm}-TS(x,T)$$
$$+\lambda\sum_{i,j,k,l,m}(n_{ijklm}-5x)z_{ijklm}(x,T)\ , \tag{7}$$

where ΔE_{ijklm} is the formation energy of the $ijklm$ configuration. In the case of the QCA the minimization of G with respect to z_{ijklm} is straightforward and gives

$$z_{ijklm}(x,T)=\frac{\zeta^{(n_{ijklm}-5x)}e^{-\Delta E_{ijklm}/k_BT}}{\sum\limits_{i,j,k,l,m}\zeta^{(n_{ijklm}-5x)}e^{-\Delta E_{ijklm}/k_BT}}\ , \tag{8}$$

where $\zeta=e^{-\lambda/k_BT}$ is a positive and real quantity, which can be determined by solving the fifth-order polynomial

$$\sum_{i,j,k,l,m}(n_{ijklm}-5x)\zeta^{(n_{ijklm}-5x)}e^{-\Delta E_{ijklm}/k_BT}=0\ . \tag{9}$$

For the case of CVM minimizing G with respect to the independent variables z_{ijklm} is more complicated and gives

$$z_{ijklm}(x,T)=\frac{X^{-5/8}Y_1^{1/2}Y_2W^{-1}\zeta^{(n_{ijklm}-5x)}e^{-\Delta E_{ijklm}/k_BT}}{\sum\limits_{i,j,k,l,m}X^{-5/8}Y_1^{1/2}Y_2W^{-1}\zeta^{(n_{ijklm}-5x)}e^{-\Delta E_{ijklm}/k_BT}}\ , \tag{10}$$

where

$$X=x_ix_jx_kx_lx_m\ ,$$
$$Y_1=y_{ij}^{(1)}y_{ik}^{(1)}y_{ij}^{(1)}y_{im}^{(1)}\ ,$$
$$Y_2=y_{jk}^{(2)}y_{jl}^{(2)}y_{jm}^{(2)}y_{kl}^{(2)}y_{km}^{(2)}y_{lm}^{(2)}\ ,$$

and

$$W=w_{ijkl}\ .$$

The subcluster variables x, $y^{(1)}$, $y^{(2)}$ and w are dependent variables which can be written in terms of the independent variables z. The system of nonlinear equations [Eq. (10)] can be solved self-consistently using the natural iteration method of Kikuchi,[26] starting with the guess values for the dependent variables and solving a fifth-order polynomial similar to Eq. (9) every iteration. Having calculated the tetrahedral concentration z, the thermodynamic functions can be calculated easily. The enthalpy of mixing is defined in Eq. (5). The entropy and the Gibbs free energy are given as in Eq. (2) [or Eq. (3)] and Eq. (4), respectively. The excess Gibbs free energy of mixing[24] is

$$G^E(x,T)=G(x,T)-k_BT[x\ \ln x+(1-x)\ln(1-x)]\ , \tag{11}$$

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the second term being the free energy of mixing of the ideal system; from $G^E(x,T)$ the interaction parameter Ω is calculated

$$\Omega(x,T)=\frac{G^E(x,T)}{x(1-x)}\ . \tag{12}$$

In I we calculated a temperature independent $\Omega(x)$, where complete randomness was assumed. In this work we have T dependence and an excess entropy contribution from the clustering effects.

As a measure for the deviation from randomness (clustering) we define the excess mixed first-neighbor pair probability distribution as the difference between the calculated distribution and the random one:

$$\Delta(x,T)=\tfrac{1}{8}\sum_{j,k,l,m}[(5-n_{1jklm})z_{1jklm}$$
$$+n_{2jklm}z_{2jklm}]-x(1-x) \tag{13}$$

which is similar to the excess mixed second-neighbor pair probability distribution used[6,29] for ternary alloys.

The stability of the disordered alloys is investigated by calculating the phase diagram (the miscibility gap and the spinodal curve) from the derivatives of the Gibbs free energy of mixing. This is the subject of the next section.

IV. RESULTS AND DISCUSSION AT $P=0$

Using the formation energy of different tetrahedral configuration calculated previously in I, the tetrahedral concentrations z_{ijklm} are calculated using Eq. (8) after solving Eq. (9) for the case of the QCA, and solving Eq. (10) self-consistently starting from a random distribution of tetrahedra. The lattice parameter $a(x)$ is assumed to vary according to Vegard's law. In principle it should be calculated by a free-energy minimization, but this is a very good approximation since the variation of a is experimentally found to be almost linear in these alloys. From the theoretical side, in I we have found that Vegard's law is very well satisfied in the periodic structures at $T=0$. Here we content ourselves by checking at $x=0.5$ that the calculated a giving minimum G is 5.491 and 5.493 Å at T equal to 100 and 300 K, respectively, compared to 5.494 Å assumed by Vegard's law. The calculated probability distribution of the different configurations of tetrahedra (i.e., the concentration z times the multiplicity factor) is shown in Fig. 1 as a function of x for different values of T. In our structural model we distinguish between the vertices and the inside sites of the tetrahedra, and as a consequence the calculated mixed first-neighbor pair concentrations are not symmetric ($y_{12}^{(1)} \neq y_{21}^{(1)}$); this does not give any problem in the case of QCA, but it does in the case of CVM, since we need to calculate $y^{(1)}$ from z to start a new iteration. To our knowledge, no solution to this problem has been proposed before. We found that by simply taking the average of $y_{12}^{(1)}$ and $y_{21}^{(1)}$ leads to unphysical results (sudden and sharp decrease in the free energy at some x). We found reasonable and satisfactory results by symmetrizing all the dependent variables when they are calculated from the variables z, by allowing each site of the basic cluster to be an inside site. In this way we allow the sites which belong to the undistorted sublattice to be inside sites.

The Gibbs free energy as a function of x at different values of T, shown in Fig. 2(a), has a quasiregular solutionlike behavior.[24] The concavity of the CVM free energy (solid curves) vanishes faster than that of the QCA (dashed curves), leading to a lower critical temperature. Even if the behavior of the CVM free energy is reasonable, the relatively large deviation from randomness at very high temperatures (see Fig. 1) could be an artifact due to the symmmetrization of the dependent variables. We finally calculated the CVM free energy in a non-self-consistent way, using in its expression simply the QCA-derived variables z. The results coincide with the one derived completely at the QCA level, thus giving us

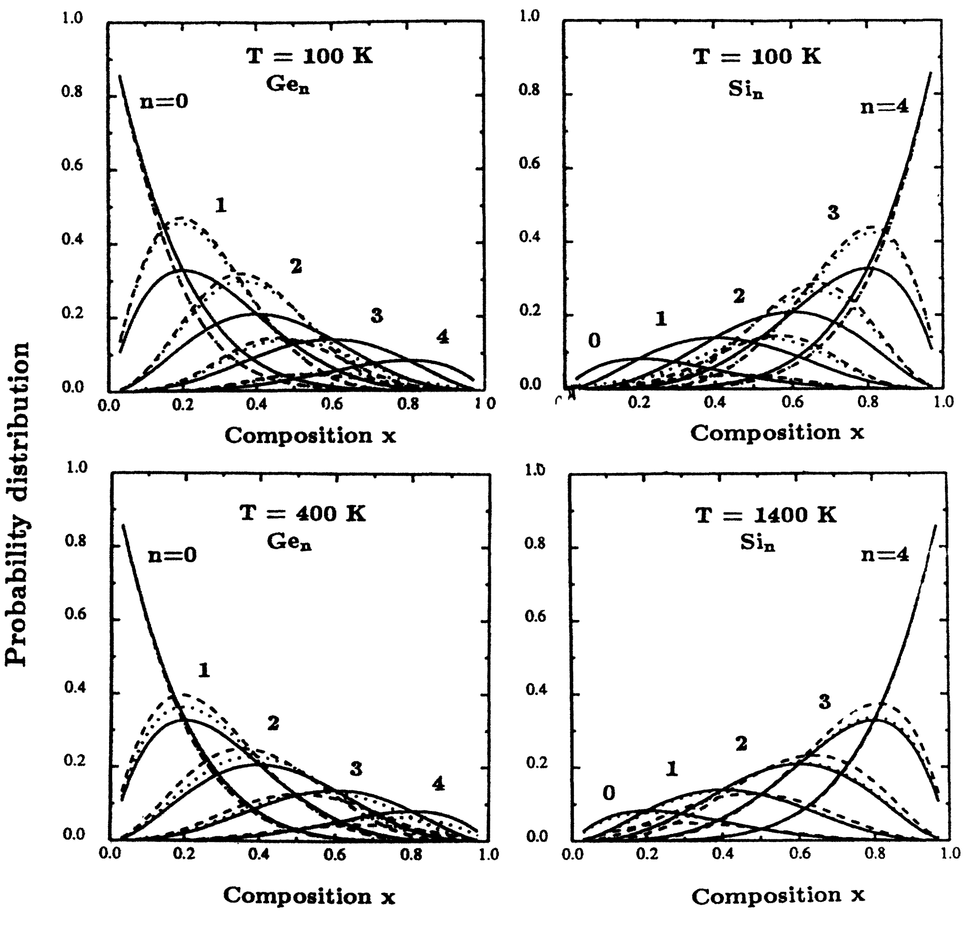

FIG. 1. The probability distribution of the tetrahedral configurations as functions of the concentration at different temperatures and $P=0$. Dashed curves, CVM results; dotted curves, QCA results, compared with the Bernoulli distribution (solid curves).

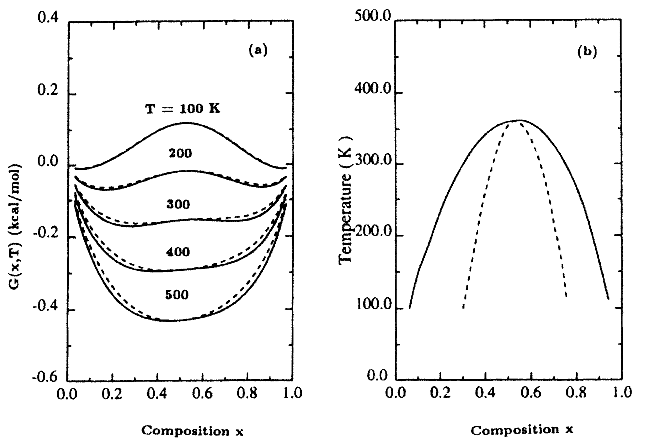

FIG. 2. (a) Gibbs free energy of mixing as functions of x at different temperatures at $P=0$. Solid curves, QCA results; dashed curves, CVM results. (b) The phase diagram of $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloys at $P=0$. Solid curve, miscibility gap; dashed curve: spinodal curve.

confidence in the accuracy and the reliability of the QCA in this system. All the results shown in the following are strictly at the QCA level.

In Fig. 2(b) the phase diagram of the disordered $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloys is shown: the instability region is where

$$\frac{\partial^2 F(x,T)}{\partial x^2}<0 \qquad (14)$$

which is bounded by the spinodal curve (dashed curve). The miscibility gap (solid curve) is by definition the region where the disordered alloys are metastable and is calculated here from the values of x at which $G(x)$ have common tangent at fixed T. The critical temperature above which the disordered alloys are stable in the whole range of x is predicted to be around 360 K [see also Fig. 2(a)]. It is evident that G and hence the phase diagram shows a regular solutionlike behavior; this is also expected from the experimental solid-liquid phase diagram[30] which demonstrates the reliability of our calculated phase diagrams. It is worth to mention again that the shown phase diagrams are calculated using QCA.

We show in Fig. 3(a) the excess free energy, enthalpy, and entropy of mixing. The dominant feature worth noting is the small values of the excess entropy, which give a small entropy contribution to G^E (the difference between the solid and the dotted curves). This fact is physically due to the small deviation of the tetrahedral distribution from complete randomness even at small temperature (see Fig. 1). As a consequence both the excess free energy G^E and the interaction parameter Ω [shown in Fig. 4(a)] have a weak T dependence.

In Fig. 5(a) we show the excess mixed first-neighbor pair probability distribution $\Delta(x,T)$: it has a negative sign near the end points and a positive one around $x=0.5$. This behavior is different from the one found in Ref. 6 for ternary alloys which is always positive, within the modified QCA. We mention also the fact that the simple (i.e., nonmodified) QCA (for ternaries) always

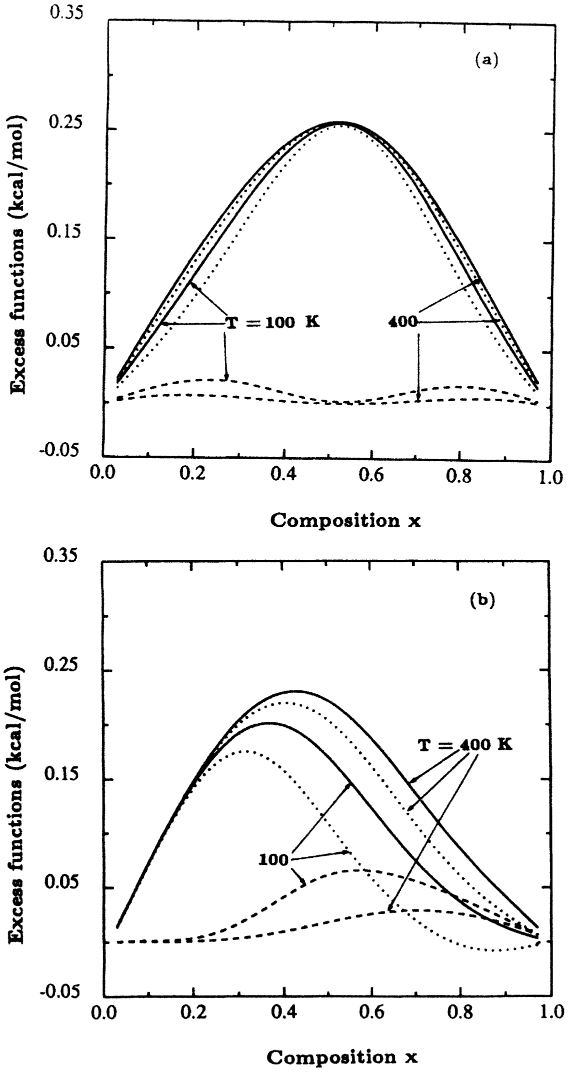

FIG. 3. Excess thermodynamic functions of mixing at $T=100$ and 400 K. At (a) $P=0$ and (b) $P=30$. Solid curve, excess Gibbs free energy; dotted curve, enthalpy; dashed curve, entropy.

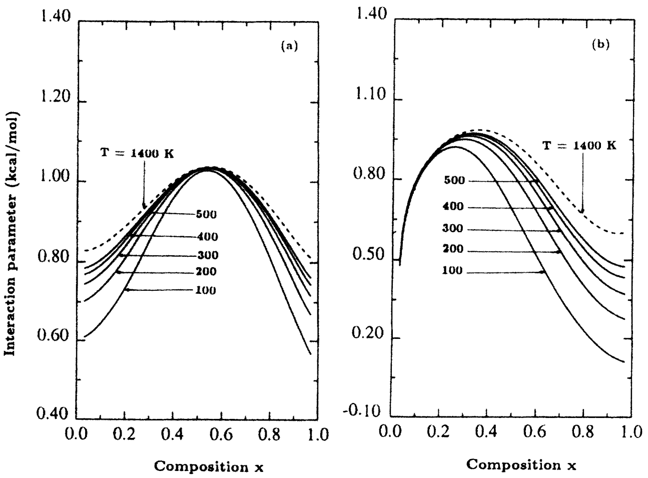

FIG. 4. Interaction parameter as a function of x at different temperatures. At (a) $P=0$ and (b) $P=30$ kbar. Solid curves, up to 500 K; dashed curve, at 1400 K (random distribution).

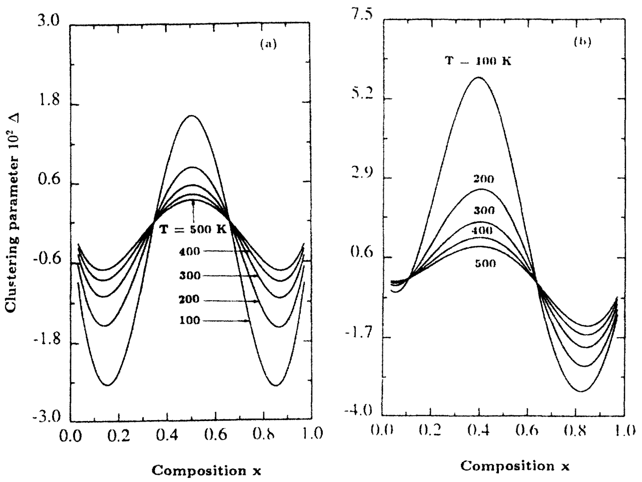

FIG. 5. Excess first-nearest-neighbor pair probability distribution Δ as function of x at different temperatures, at (a) $P=0$ and (b) $P=30$ kbar.

gives a negative deviation.[29] The behavior of Δ in our case can be easily understood. For example, in the Si-rich side the Si-rich tetrahedra have less strain (positive) energy, which tends to increase their probability distribution [see Fig. (1)]. As a consequence the values of $y^{(1)}_{\rm SiSi}$ increases on the expense of $y^{(1)}_{\rm SiGe}$ and $y^{(1)}_{\rm GeGe}$. Therefore the negative sign of Δ near the end points is explained. The same arguments can be used to explain the positive sign of Δ around $x=0.5$. The small tendency to clustering (Δ is 1 order of magnitude smaller than the values calculated for ternary alloys), i.e., small tendency to ordering in these materials, provides further support to the conclusion of the instability of any coherent structure for bulk $\mathrm{Si}_x\mathrm{Ge}_{1-z}$ alloys.

V. THE PRESSURE EFFECTS

The results reported so far are obtained at $P=0$. In this section we will study the effects of applying a hydrostatic pressure on the thermodynamic properties. The lattice parameter a of Si and Ge at given P can be determined from the calculated equations of state. Here we will also assume a Vegard's-law variation of $a(x)$ between the calculated values of Si and Ge at the same P. The formation energies of each kind of tetrahedra at fixed T are recalculated according to.

$$\Delta E_{A_n}(x,P)=E_{A_n}(a(x,P)) - \left[\frac{4+n}{8}E_A(P)+\frac{4-n}{8}E_B(P)\right] \qquad (15)$$

and similarly for ΔE_{B_n}, where $E_A(P)$ and $E_B(P)$ are the

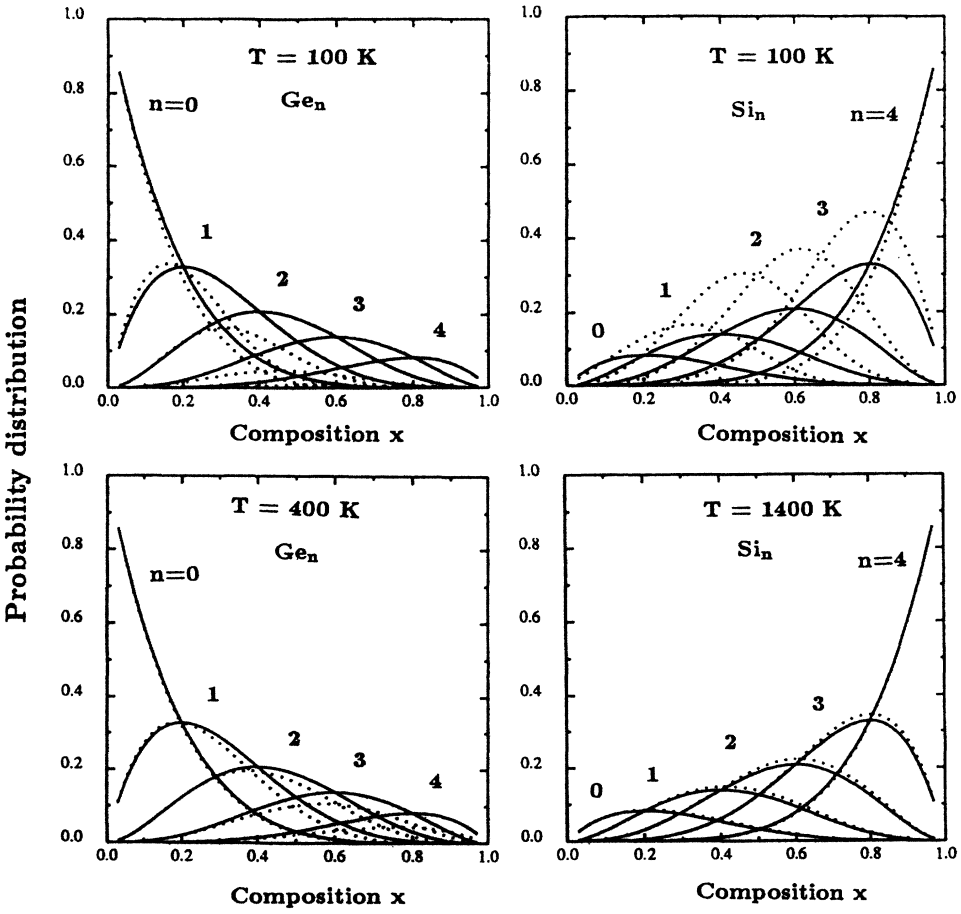

FIG. 6. The probability distribution of the tetrahedral configurations as functions of the concentration at different temperatures and $P=30$ kbar. Dotted curves; QCA results, compared with the Bernoulli distribution (solid curves).

total energies of the end materials under fixed P. We found that ΔE of the ordered structures decreases by increasing the pressure, but this reduction is not enough to stabilize them (e.g., ΔE for zinc-blende structure is 0.68, 0.66, 0.60, and 0.51 mRy/atom under 0, 50, 70, and 90 kbar, respectively). Our prediction is therefore that isotropic pressure does not make this compound stable; we comment at this point that uniaxial strain on the contrary has been recently found to stabilize ordered structures in these materials.[31,32]

At given P the calculations of the thermodynamic properties are carried out as described before, using the formation energies calculated at the same P. As a consequence of the volume reduction by applying hydrostatic pressure, the strain energy of the Ge-rich tetrahedra increases. Therefore, the probability distribution of the Si-rich tetrahedra will increase because they have less strain energy.

For the purpose of displaying, all the following results are shown at $P=30$ kbar. The probability distributions at different temperatures as functions of x are shown in Fig. 6; by comparing it to Fig. 1 we see the pressure-induced change in the probability distributions of Si_n and Ge_n clusters, which has a direct effect on the thermodynamic properties. In Fig. 3(b) we show the calculated excess Gibbs free energy, enthalpy, and entropy of mixing, to be compared with the zero-pressure behavior shown in Fig. 3(a). The interaction parameter at different values of T as functions of x is shown in Fig. 4(b) [notice the difference in scale in Fig. 4(a) and 4(b)]. The dominant feature to be noticed is the relatively strong T dependence in the Si-rich side and the T independence in the Ge-rich side, the same feature existing also in Fig. 3(b) for the thermodynamic functions.

The Gibbs free energy at different values of T is shown in Fig. 7(a); this quantity is in general lower than at $P=0$, having a larger difference in the Si-rich side, and it is mainly due to a reduction in the enthalpy of mixing. The corresponding phase diagram is shown in Fig. 7(b), where the effects of the pressure on the phase diagram can be seen: the main effect is that the instability region moves toward the Ge-rich side and its width decreases. We show in Fig. 8 the critical temperature as a function of P. The behavior is a monotonical increase of $T_c(P)$ with a rather small derivative at pressure up to about 50 kbar and a steeper increase beyond. This can be understood since the total energy is flat around the equilibrium volumes.

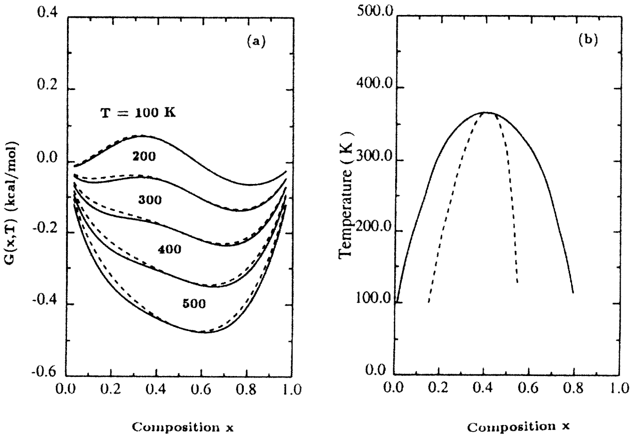

FIG. 7. (a) Gibbs free energy of mixing as functions of x at different temperatures at $P=30$ kbar. Solid curves, QCA results; dashed curves, CVM results. (b) The phase diagram of $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloys at $P=30$ kbar. Solid curves, miscibility gap; dashed curve, spinodal curve.

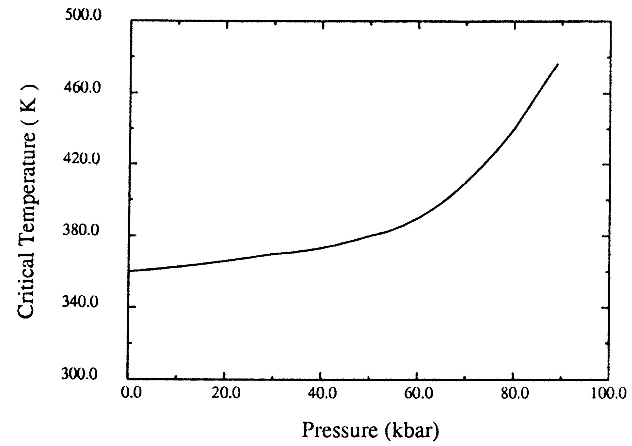

FIG. 8. The critical temperature as a function of the pressure.

In Fig. 5(b) we show Δ at different values of T as a function of x. We found therefore that the pressure has also a drastic effect on the clustering in these materials, because Δ is no more symmetric, and the tendency to clustering increases [notice the change in scale in Figs. 5(a) and 5(b)]. This behavior can be explained as a consequence of the change in the role played by the strain energy.

VI. CONCLUSIONS

A combined electronic-structure and statistical-mechanical approach has been used to calculate the thermodynamic properties of $\mathrm{Si}_x\mathrm{Ge}_{1-x}$ alloys. The formation energy for each of the five-site tetrahedral configurations have been calculate using the local-density approximation and norm-conserving pseudopotentials, whereas an approximate entropy of mixing is calculated within the framework of the modified QCA and CVM. We draw the following main conclusions.

1. Because of our structural model which distinguishes the inside site from the others, the calculated mixed first-neighbor pair concentration is not symmetric. The CVM calculations are carried out by symmetrizing all the dependent variables; this leads to unphysical deviation of the CVM probability distributions from randomness at very high temperatures. However, we found that the QCA free energy coincides with that of CVM calculated using the same QCA probability distributions, which demonstrates the power and the reliability of the QCA. The following conclusions are based on this approximation.

2. The Gibbs free energy shows a regular solutionlike behavior, and the critical temperature above which the disordered alloy is stable for the whole range of concentration is predicted to be around 360 K.

3. The interaction parameter shows a weak temperature dependence specially around room temperature, in addition to the weak concentration dependence previously found.

4. The tendency to clustering is found to be much smaller than that calculated for ternary alloys,[6] which provides additional support for the instability of ordered bulk Si_xGe_{1-x} structures.

5. The pressure has a sizable effect on the thermodynamic functions and clustering. The pressure tends to decrease the width and to shift the instability region toward the Ge-rich side; the critical temperature increases by increasing the pressure.

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