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Phase diagram of the $Fe_{1-x}Co_xSi_2$ alloy in the fluorite form

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The phase diagram of the $Fe_{1-x}Co_xSi_2$ alloy in the fluorite form has been computed from first principles. The alloy has been represented as an ensemble of tetrahedral clusters in which the corners are occupied by Fe or Co atoms in five possible configurations around a central Si atom. The formation energy of each cluster as a function of the lattice constant has been evaluated by means of self-consistent total-energy calculations of the corresponding ordered structure based on the linear muffin-tin orbitals method within the density-functional theory. Using the cluster-variation method for the evaluation of the entropy, we have obtained the phase diagram, showing that a disordered $Fe_{1-x}Co_xSi_2$ alloy (in fluorite form) could be easily grown above 160 K. We have also fitted the total energies of the end compounds to derive the bond-stretching constants α_{FeSi_2} and α_{CoSi_2}. Through these quantities and an elastic model of the alloy we have evaluated the displacement of the Si atom from the center of each tetrahedron and the mean Fe-Si and Co-Si distances as a function of the concentration. The energy connected to this relaxation has been subtracted from the previously obtained formation energies, leading to a final value of the critical temperature ($T_c = 115$ K) definitely lower than the previous one. This fact confirms the importance of the internal relaxation also in systems with small lattice mismatch.

I. INTRODUCTION

The rush towards developing new optoelectronic materials has drawn the attention of researchers to alloys of transition metals with silicon, with the intention of integrating the sensor and the electronic circuits on the same chip. For these purposes the optimum candidate is the $FeSi_2$ alloy in its low-temperature (β) form,[1] a semiconductor that could be mixed with one of the other metallic disilicides to control the energy gap in the whole infrared region.

$FeSi_2$ and $CoSi_2$ mixing is known to generate an alloy which has a complicated phase diagram. In fact, while the $CoSi_2$ is stable in the fluorite form (Fig. 1), the β-$FeSi_2$ structure is orthorhombic[2,3] (Fig. 2), but it could be viewed as a distorted fluorite structure. Owing to these differences a very limited mutual solubility of these disilicides has been reported.[4] From the $FeSi_2$ side, solubility up to 10% of $CoSi_2$ has been reported in the β form. To start the investigation on this phase diagram, we have simplifed the approach, treating the two systems as having both the same (fluorite) structure. In this way, the resulting $Fe_{1-x}Co_xSi_2$ alloy keeps this structure with x Fe atoms replaced by Co atoms.[5]

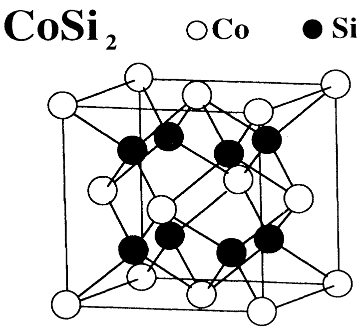

FIG. 1. The $CoSi_2$ structure (fluorite). Open circles represent Co atoms. Solid circles represent Si atoms.

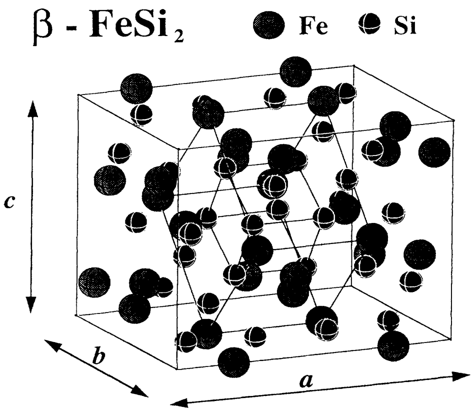

FIG. 2. The β-$FeSi_2$ structure. Shaded circles represent Fe atoms. Solid circles represent Si atoms.

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II. CLUSTER ENERGY CALCULATION

It is well known that when an atom in a crystal structure is replaced by another of a different kind, a certain amount of energy η is needed to relax the crystal around the impurity (*elastic energy*) and to rearrange the chemical bonds (*chemical energy*). Of course, this energy depends mainly on the environment of the substituted atom. In order to simplify the problem, the $Fe_{1-x}Co_xSi_2$ alloy has been described by taking the tetrahedra as building blocks (there are eight of these tetrahedra for each cube of lattice parameter a). At the center of each tetrahedron there is a Si atom, while its corners are occupied by Fe and Co atoms in five possible configurations. Each of them comes from an ordered crystal of $Fe_{4-n}Co_nSi_8$, type as shown in Fig. 3.

The energy of each tetrahedron has been evaluated from a self-consistent total-energy calculation of the corresponding ordered crystal. The calculation of the ordered structures was performed by using the (relativistic) linear muffin-tin orbitals (LMTO) method[6] in conjunction with the local-density approximation to density-functional theory. The LMTO calculations were optimized by inserting[7] four *empty spheres* in the cell containing eight Si atoms. The total energies were, for each compound and at each volume, calculated from self-consistent-field (SCF) band-structure calculations using identical geometries in real as well as in reciprocal space, i.e., the same number of atoms and the same mesh of k points used for Brillouin-zone integrations. The number of k points was gradually increased until the numerical error in structural energy differences was well below 1 mRy.[8] By this we mean that we first performed a com-

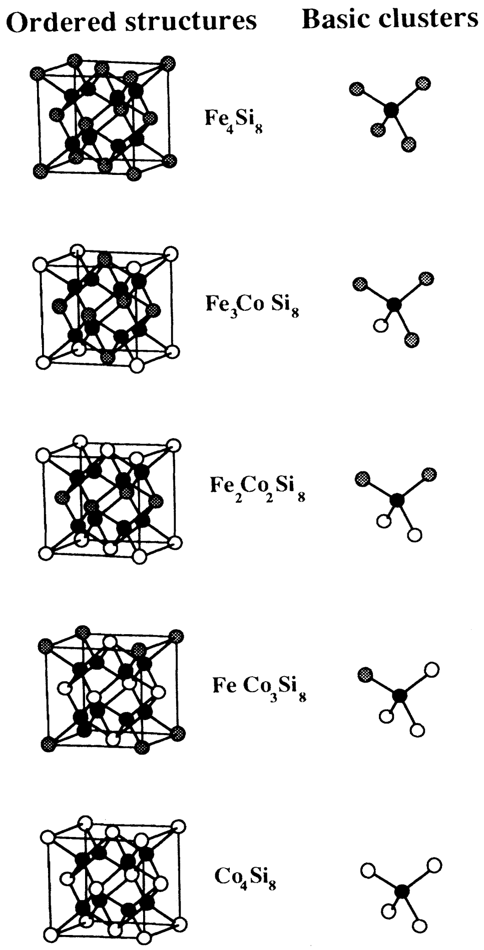

FIG. 3. The five ordered structures and the basic clusters of $Fe_{4-n}Co_nSi_8$ in the fluorite form.

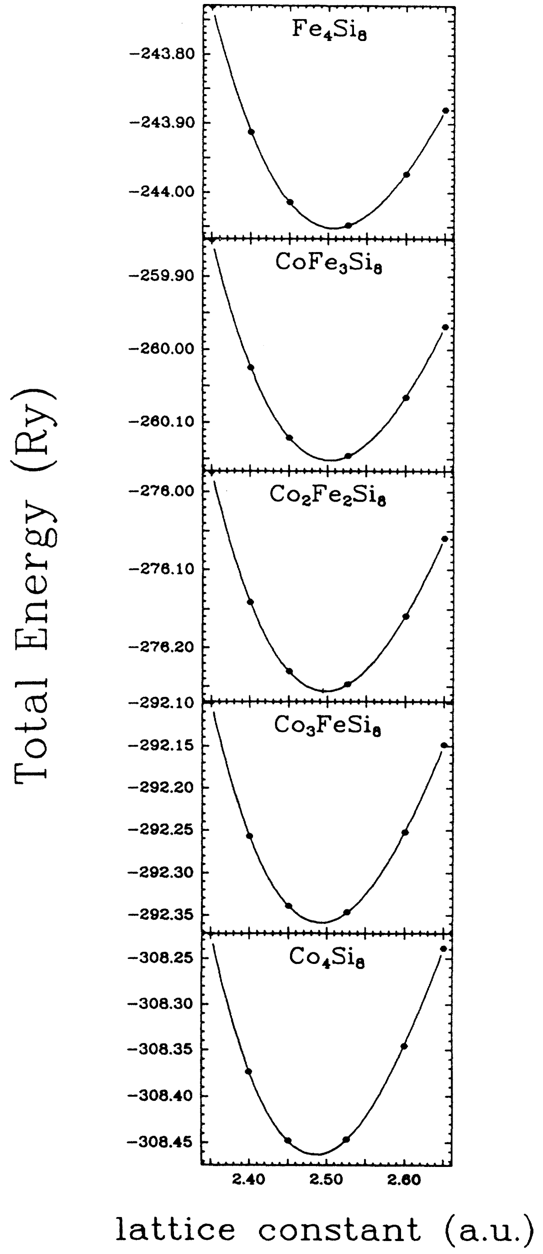

FIG. 4. The total valence energies of the five configurations. The self-consistently calculated points were fitted with a cubic spline (rms error 10^{-6}). The energies at the minima are (in Ry) -244.0520 for Fe_4Si_8, -260.1524 for $n=1$, -276.2559 for $n=2$, -292.3589 for $n=3$, and -308.4632 for Co_4Si_8.

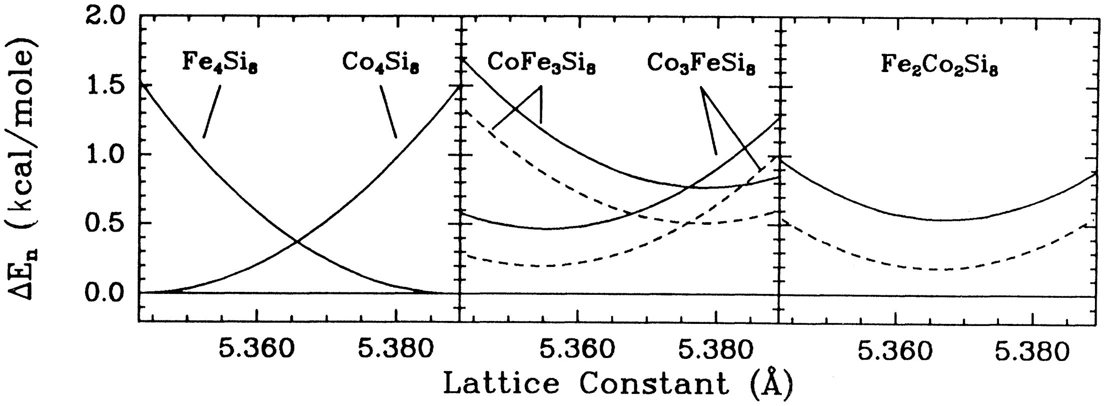

FIG. 5. The formation energies of the five clusters: unrelaxed—from the self-consistent calculations (solid lines)—and relaxed—after removal of the extra elastic energy (dashed lines).

plete series of total-energy calculations using only 22 special k points. We then repeated all the calculations (i.e., for all compounds and at all volumes) using 45 k points in the irreducible zone. At all volumes the relative energy position of any compound as compared to any other compound changed by less than 1 mRy per cell (a "cell" containing eight Si atoms). As a further check of the numerical stability, we then recalculated the energy-volume curves for selected compounds using 76 k points. When compared to the 45-k-point calculations, the increased number of k points led to increases in the total energy by amounts that vary smoothly with volume, and lie between 0.3 and 0.7 mRy/cell. The relative position of energy curves change by less than 0.2 mRy/cell. Thus, k-space integration errors are ≈ 1 mRy/cell in the total energies themselves, but below ≈ 0.2 mRy/cell in the differences, i.e., the quantities that matter in the present application. Errors due to finite numbers of iterations toward self-consistency are negligible; the total energies are converged to 10^{-6} Ry and the Madelung energies of 10^{-5} Ry (which is a measure of convergence of the charge distribution). These latter numbers refer to an iteration scheme where linear mixing of charge densities at the last 10–12 cycles uses a feedback of 75–80 %.

When a tetrahedron is inserted in the disordered structure with $a=a(x)$, its volume is relaxed so that its corners (Fe or Co) match the ideal crystal position at that lattice parameter. No displacement from the center of the tetrahedron was allowed for the Si atoms. This approximation is somewhat crude as compared to the calculation by Qteish *et al.*,[9] which did include this kind of relaxation. However, the differences in lattice parameters of the $CoSi_2$ and (theoretical) $FeSi_2$ are so small that only minor errors are expected (this approximation will be reconsidered in Sec. IV). The results of the total energy versus a of the five configurations are shown in Fig. 4, along with a cubic spline fitting. To get the formation energy for each structure, the total energy of the pure materials $CoSi_2$ and $FeSi_2$ has been subtracted (Fig. 5):

$$\Delta E_n(a)=E_n(a)-\left[\frac{4-n}{4}E_{\mathrm{FeSi}_2}+\frac{n}{4}E_{\mathrm{CoSi}_2}\right], \qquad n=0,\ldots,4 . \qquad (1)$$

Finally, the correspondence between the latter parameter and the composition has been derived by use of Vegard's law:

$$a(x)=a_{\mathrm{FeSi}_2}+(a_{\mathrm{CoSi}_2}-a_{\mathrm{FeSi}_2})x .$$

This assumed linear dependence agrees very well with the variation of the lattice parameter derived from the total-energy minimization for the ordered structures (Fig. 6).

III. BUILDING THE PHASE DIAGRAM

The phase diagram is obtained from the minimization of the Gibbs free energy of mixing,

$$\mathrm{G_m}(x,T)=\mathrm{H_m}(x,T)-T\mathrm{S}_m(x,T) . \qquad (2)$$

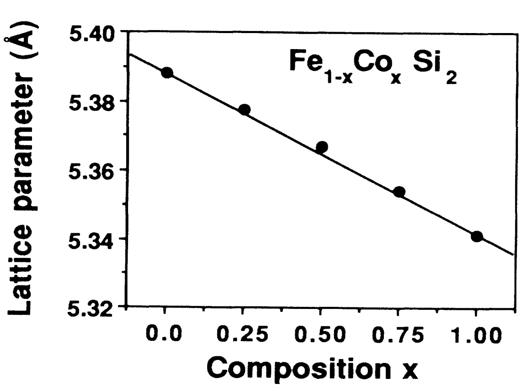

FIG. 6. Equilibrium lattice constants of the five ordered $Fe_{4-n}Co_nSi_8$ configurations (dots) compared to Vegard's law (solid line).

From the cluster energies we compute the enthalpy of mixing,[10]

$$\mathbf{H}_{\mathrm{m}}(x,T)=\sum_{n=0}^{4} P_n(x,T)\Delta E_n(x,T) \ . \tag{3}$$

Here, P_n is the four-site tetrahedron probability and summation is over all its possible configurations. In order to derive the probability, we write relation (3) as

$$\mathbf{H}_{\mathrm{m}}(x,T)=\sum_{i,j,k,l=0}^{1} z_{ijkl}\Delta E_{ijkl} \ , \tag{4}$$

where $P_n \rightarrow z_{ijkl}$ and $\Delta E_n \rightarrow \Delta E_{ijkl}$. The correspondence between n and $ijkl$ is given by

$$n=i+j+k+l$$
$$(i,j,k,l=1 \text{ for Co atom and 0 for Fe}) \ . \tag{5}$$

With this prescription, n equals the number of Co atoms in the tetrahedron. The configurational entropy $\mathbf{S}_m$ is also a function of the basic cluster concentration z. Following the cluster-variation method (CVM) of Kikuchi,[11] the entropy for the four-site tetrahedron is given as

$$\mathbf{S}_{\mathrm{m}}=-k_B\left[5\sum_i x_i \ln x_i - 6\sum_{i,j} x_{ij}^{(2)}\ln x_{ij}^{(2)} + 2\sum_{i,j,k,l} z_{ijkl}\ln z_{ijkl}\right] , \tag{6}$$

where x_i denotes the site concentration and $x_{ij}^{(2)}$ denotes the concentration of the next-nearest-neighbor pairs Fe-Co. The Gibbs free energy of mixing, $\mathbf{G}_{\mathrm{m}}$, can be minimized with respect to the independent variables z to calculate $\mathbf{G}_{\mathrm{m}}^{\mathrm{eq}}$, z_{ijkl}, and $\mathbf{S}_m$, from which the other thermodynamic functions can be easily determined. This has to be done under the constraint

$$\sum_{i,j,k,l} (n-4x)z_{ijkl}=0 \ , \tag{7}$$

which takes into account both the fixed concentration and the normalization condition (the sum of the variables z is equal to 1). Therefore, the free energy of mixing to be minimized is

$$\mathbf{G}_{\mathrm{m}}(x,T)=\sum_{i,j,k,l} z_{ijkl}(x,T)\Delta E_{ijkl} - T\mathbf{S}_{\mathrm{m}}(x,T)+\lambda\sum_{i,j,k,l}(n-4x)z_{ijkl}(x,T) \ , \tag{8}$$

where the formation energies, ΔE_{ijkl}, are calculated according to Eq. (1) and λ is a Lagrange multiplier. The system of nonlinear equations, Eq. (8), can be solved self-consistently using the natural iteration method of Kikuchi,[11] starting with guessed values of the dependent variables and solving a fourth-order polynomial during each iteration. From the equilibrium Gibbs free energy, $\mathbf{G}_{\mathrm{m}}^{\mathrm{eq}}$, the phase diagram (miscibility gap and spinodal curve) are derived. In Fig. 7 the $\mathbf{G}_{\mathrm{m}}^{\mathrm{eq}}(x,T)$ functions for $Fe_{1-x}Co_xSi_2$ are shown for different T ranging from 110 to 150 K. The instability region in (x,T) space, bounded by the spinodal curve, is the region where

$$\frac{\partial^2 \mathbf{G}_{\mathrm{m}}^{\mathrm{eq}}(x,T)}{\partial x^2}<0 \ , \tag{9}$$

while the miscibility gap, above which the disordered alloy is stable [Fig. 8(a)], can be calculated from the values of x at which $\mathbf{G}_{\mathrm{m}}^{\mathrm{eq}}(x)$ have common tangent at fixed T. It can be noticed that the critical temperature (the maximum of the curve) is at 160 K. This is the minimal temperature at which the alloy can be treated at any concentration in a homogeneous form. Such a low critical temperature is due to the fact that the Fe and Co atoms are so similar in size that it is very easy to create the alloy. However, it is interesting to see that the maximum of the curve does not correspond to $x=0.5$, which means that the alloy is not ideal, and interactions between next-nearest neighbors are not negligible.[12]

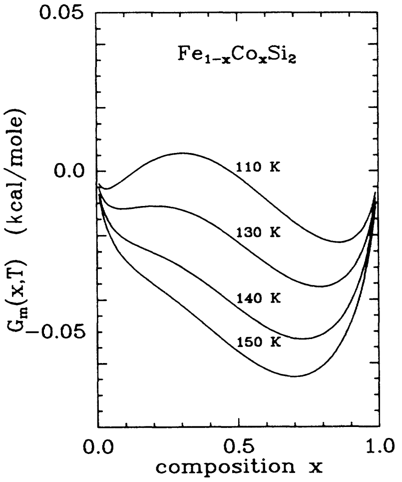

FIG. 7. Gibbs free energy of mixing of the $Fe_{1-x}Co_xSi_2$ alloy at different temperatures.

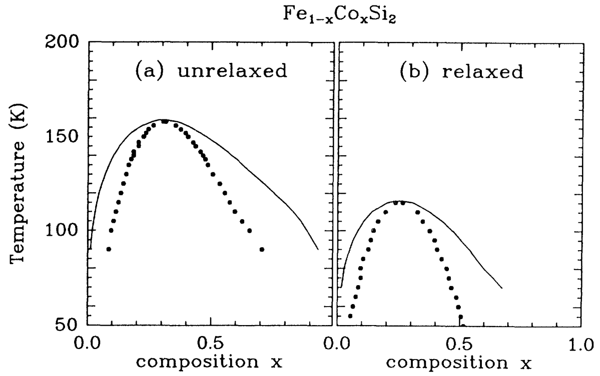

FIG. 8. Theoretical phase diagram of $Fe_{1-x}Co_xSi_2$ in the fluorite form: (a) unrelaxed model and (b) relaxed model (see Sec. IV).

IV. CENTRAL-ATOM RELAXATION AND NN DISTANCES

In the total-energy calculation only the volume of the cell was changed, without relaxing the position of the internal Si atom. In order to see how much the Si atom is displaced from its position at the center of the tetrahedron and to compute the nearest-neighbor (NN) distances, one can use the Keating model.[13] Following this model, and assuming for the metal silicides approximately the same behavior of the zinc-blende semiconductors, we can represent the elastic energy of the tetrahedra in the form[14]

$$\eta_n(a)=n\tfrac{3}{8}\alpha_{\mathrm{CoSi}_2}\frac{(y_n^2-y_0^2)^2}{y_0^2}+(4-n)\tfrac{3}{8}\alpha_{\mathrm{FeSi}_2}\frac{(z_n^2-z_0^2)^2}{z_0^2}\ , \tag{10}$$

where y_n and z_n are the actual Co-Si and Fe-Si distances in the tetrahedron with n Co atoms, y_0 and z_0 are the ideal distances in the pure materials, and α_{CoSi_2} and α_{FeSi_2} are the bond-stretching constants. By fitting the previously computed total-energy curves with the formula

$$E(a)=\alpha\frac{9}{16}\frac{(a^2-a_0^2)^2}{a_0^2}+\mathrm{const}\ , \tag{11}$$

we find[15] $\alpha_{\mathrm{CoSi}_2}=53.8$ N m/Å^2 and $\alpha_{\mathrm{FeSi}_2}=59.1$ N m/Å^2 (no experimental data are available for the bond-stretching constants of CoSi_2 and FeSi_2). Now the y_n and z_n can be obtained by the minimization of (10), and the mean value of Co-Si and Fe-Si distances in the alloy are given by

$$R_{\text{Co-Si}}(x)=\sum_n P_n(x)y_n(x)\ ,$$

$$R_{\text{Fe-Si}}(x)=\sum_n P_n(x)z_n(x)\ ,$$

where the $P_n(x)$ correspond to the z_{ijkl} obtained in the phase-diagram calculation at $T=T_f$ (formation temperature of the alloy).[16] The result is shown in Fig. 9, which clearly exhibits the splitting of the Fe-Si and Co-Si NN distances as a function of x. The mean of the two distances (Vegard's law) is also compared to the distances obtained from the total-energy calculation (dots), showing perfect agreement.

Now we are in the position to improve the mixing energies calculated in Sec. II by subtracting the elastic energy associated with the relaxation of the Si-atom positions. The energies corresponding to the equilibrium lattice parameter (formation energy) for the relaxed structures can now be considered purely chemical,[17] because any elastic term has been removed (see Table I). By using these corrected energies, a new phase diagram has been obtained, which looks qualitatively like the one already shown, but with a critical temperature of 115 K [Fig. 8(b)]. This reduction of T_c does not alter our general conclusions about the phase diagram. However, one should note that, even for this system, where one would expect, *a priori*, very little importance of the internal relaxations, they nevertheless alter the key parameters of the phase diagram significantly.

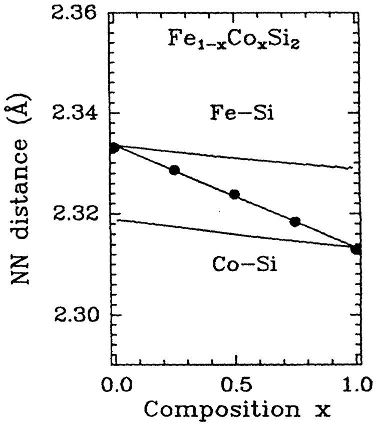

FIG. 9. NN distances in $\mathrm{Fe_{1-x}Co_xSi_2}$ from the elastic model (lines) and from the self-consistent unrelaxed calculation (dots).

V. CONCLUSIONS

We performed a self-consistent total-energy calculation of the five possible $\mathrm{Fe_{4-n}Co_nSi_8}$ structures in the fluorite form at different values of the lattice parameter a. The formation energy of each structure was obtained by calculating its difference from that of the pure materials. The phase diagram was obtained by taking the tetrahedra as the basic clusters in the CVM approximation, and from the computed mixing energies. A miscibility gap appears only under $T=160$ K. This means that a disordered $\mathrm{Fe_{1-x}Co_xSi_2}$ alloy (in the fluorite form) could be easily grown above this temperature. The NN distances were computed within an elastic model by using the bond-stretching constants derived from the total energies. The resulting Fe-Si and Co-Si mean distances differ by about 2×10^{-2} Å. The energy lowering connected to

TABLE I. Lattice constants and formation energies of the five $\mathrm{Fe_{4-n}Co_nSi_8}$ ordered structures. One mole is referred to the given chemical formula (full unit with eight Si atoms). The relaxed formation energies are computed by subtracting the elastic energy associated with the displacement of the central atom.

Compound	Lattice constant (Å)	Formation energy (kcal/mol) Unrelaxed	Relaxed
$\mathrm{Fe_4Si_8}$	5.3885	0	0
$\mathrm{CoFe_3Si_8}$	5.3780	0.77	0.47
$\mathrm{Co_2Fe_2Si_8}$	5.3675	0.54	0.18
$\mathrm{Co_3FeSi_8}$	5.3555	0.47	0.20
$\mathrm{Co_4Si_8}$	5.3435	0	0

these relaxations has been included in the thermodynamic model, obtaining a non-negligible reduction of the critical temperature.

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[1] N. Cherief, C. D'Anterroches, R. C. Cinti, T. A. Nguyen Tan, and J. Derrien, Appl. Phys. Lett. **55**, 1671 (1989).

[2] P. Y. Dusausoy, J. Protas, R. Wandji, and B. Roques, Acta Crystallogr. Sect. B **27**, 1209 (1971).

[3] O. Kubachewski, *Iron-Binary Phase Diagrams* (Springer-Verlag, New York, 1982), pp. 136–139. (Note that, contrary to the definition of this reference, we have identified the $FeSi_2$ orthorhombic phase as β according to the more usual prescription of Refs. 1 and 2.)

[4] A. Wittmann, K. O. Burger, and H. Nowotny, Monatsh. Chem. **92**, 961 (1961).

[5] Although this approach can appear to be far from reality, it is a very useful simplification to understand the basics of this complex material.

[6] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[7] W. R. L. Lambrecht, N. E. Christensen, and P. Blochl, Phys. Rev. B **36**, 2493 (1987), and references therein.

[8] N. E. Christensen, S. H. Wei, and A. Zunger, Phys. Rev. B **40**, 1642 (1989); N. E. Christensen, Solid State Commun. **68**, 959 (1988).

[9] A. Qteish, N. Motta, and A. Balzarotti, Phys. Rev. B **39**, 5987 (1989).

[10] One tetrahedron corresponds to $\frac{1}{2}$ mole in a fluorite MSi_2 structure. So the ΔE_n considered here for 1 mole, in fact, correspond to two tetrahedra. This, however, is consistent with the successive evaluation of the entropy.

[11] R. Kikuchi, J. Chem. Phys. **60**, 1071 (1974).

[12] D. De Fontaine, in *Solid State Physics: Configurational Thermodynamics of Solid Solutions,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1979), Vol. 34, p. 73.

[13] P. N. Keating, Phys. Rev. **145**, 637 (1966).

[14] A. Balzarotti, A. Kisiel, N. Motta, M. Zimnal-Starnawska, M. Czyzyk, and M. Podgorny, Phys. Rev. B **31**, 7526 (1985).

[15] The bond-stretching constants computed in this way have the same meaning as in the Keating model for the diamond structure. In fact, one has to sum over eight bonds (two tetrahedra) to get the molar energy for the fluorite structure.

[16] We have assumed $T_f = 900$ K, which is the formation temperature of both $FeSi_2$ and $CoSi_2$ by solid-phase epitaxy. [See also J. Y. Veuillen, T. T. A. Nguyên, R. Cinti, M. De Crescenzi, and J. Derrien, Phys. Rev. B **39**, 8015 (1989).] However, due to the small mixing enthalpy, at this temperature the $P_n(x)$ coincides with the random one.

[17] L. G. Ferreira, A. A. Mbaye, and A. Zunger, Phys. Rev B **37**, 10 547 (1988); L. G. Ferreira, S. H. Wei, and A. Zunger, *ibid.* **40**, 3197 (1989).