

First principles prediction of the metastability of the Ge₂Mn phase and its synthesis pathways

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In this letter, we performed first principles calculations to investigate the stability of a [100]-compatible Ge₂Mn compound. Based on a thermodynamical approach, we propose and assess the C16 structure (Al₂Cu prototype) to be only slightly metastable as compared to the other Ge–Mn compounds. The reported structural and magnetic properties of this Ge₂Mn compound make it a potentially interesting compound for spintronic applications, all the more since a simple way to stabilize it as a bulk film is proposed. © 2010 American Institute of Physics.

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Spin injection into semiconductor is a key issue for spintronics in order to take advantage of the silicon-based electronics. The intermetallic compound Ge₃Mn₅ has been considered for a few couple of years as a promising candidate for spin injector for semiconductor because of (i) its good lattice match with silicon-based materials, (ii) its high Curie temperature (T_C), tunable through carbon doping,¹ and (iii) its rather good spin polarization.² However the growth of this compound is only possible on a [111] diamond-like substrate while silicon electronics is mostly based on [001] substrates. This drawback makes the stabilization of a [001]-compatible GeMn compound a major issue of spintronics.

On the other hand, many attempts have been made to obtain a room-temperature diluted magnetic semiconductor (DMS), using molecular beam epitaxy³ (MBE) or Mn implantation.⁴ However, the low solubility of Mn in Ge always leads to a phase separation into pure Ge and Mn-rich clusters, even at low Mn content. Many types of known compounds have been reported as the precipitates, such as Ge₈Mn₁₁, Ge₃Mn₅, or Ge₂Mn₅.⁵ However, a Ge₂Mn secondary phase was also reported by Jamet *et al.*,⁶ that clusterizes into nanocolumns coherent with the Ge diamond matrix.

These observations of Jamet *et al.*⁶ are somewhat unexpected and deserve a detailed theoretical analysis of the Ge–Mn phase diagram. In this letter, we have performed density functional theory (DFT) calculations to investigate the possibility to stabilize a Ge₂Mn bulk compound compatible with [100] substrates. Based on these calculations we propose a yet unknown Ge₂Mn compound along with a simple synthesis pathways to stabilize it as a bulk film.

We have used the projector augmented-wave (PAW) approach as implemented in the ABINIT code,⁷ within the generalized gradient approximation⁸ (GGA) for the exchange-correlation energy. GGA+U framework was not used because of the inherent difficulty in total energy comparisons. Pseudopotentials were generated to ensure completeness of the PAW basis set. The electrons taken into account as valence electrons are 4s and 4p for Ge and 4s and 3d for Mn. Using different **k**-points sampling for each of the considered compounds, we ensured the convergence of the total energy with respect to the number of sampling points better

than 10⁻³ eV per atom. This allowed us to directly compare the energies for the unit cells of different shapes and sizes. For each system the unit cell vectors and internal coordinates were fully relaxed at a given collinear spin configuration in a self-consistent way.

The Ge_{1-y}Mn_y phase diagram⁹ shows only six stable compounds at zero temperature. We are interested here in those with the higher Ge content (see Fig. 1) which appear in the phase segregation of GeMn films as follows: (i) the diamond Ge ($y=0$, cubic $Fd\bar{3}m$ symmetry); (ii) Ge₈Mn₁₁ (Ref. 10) ($y=0.58$, orthorhombic Pnm symmetry); (iii) Ge₃Mn₅ (Ref. 11) ($y=0.63$, hexagonal $P6_3/mcm$ symmetry, D8₈-type structure); and (iv) Ge₂Mn₅ (Ref. 12) ($y=0.71$, orthorhombic $Ibam$ symmetry). In addition to these known phases, we supplement the phase diagram with a Ge₂Mn compound with C16-type structure ($y=0.33$, tetragonal $I4/mcm$ symmetry). The nonprimitive unit cell contains 12 atoms; four Mn at 4(*a*) and eight Ge at 8(*h*) positions, the latter being further defined by the reduced parameter x .¹³

This compound is inspired by experiments of Regan *et al.*,¹⁴ which show similar anisotropic phase separations in Fe–Ge systems as in experiments of Jamet *et al.*,⁶ with an iron concentration of 30%–40% in the Fe-rich regions, i.e., close to the stable FeGe₂ composition. Thus, we considered

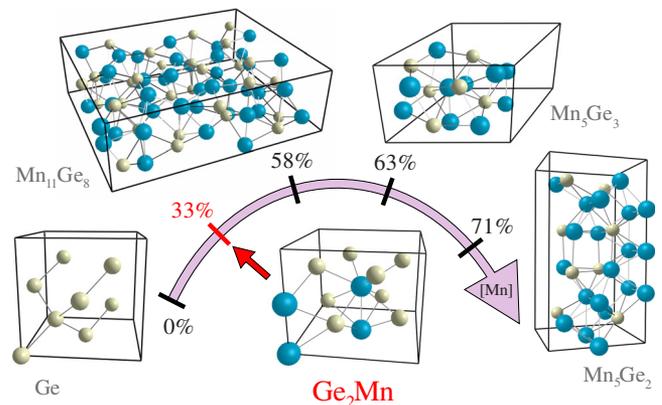


FIG. 1. (Color online) The four Ge-richer known compounds of the Ge–Mn phase diagram, stable at zero temperature, with the Mn concentration ranging from 0% to 71%. Although there is no stable compound between 0% and 58% of Mn, we supplement the diagram with Ge₂Mn, corresponding to the Mn concentration of 33%.

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the possibility of substituting Fe by Mn in the C16 structure. Such substitution by Mn (and Co) has been considered in a previous *ab initio* study.¹⁵ However, neither stability of Ge₂Mn with respect to the other known Ge–Mn phases, nor its transition temperature has been studied. Before discussing the bulk properties of this proposed compound, we will assess its energetic stability by a thermodynamic study.

First, for all four stable compounds (see Fig. 1) we have calculated the ground-state structural and magnetic configurations by fully relaxing the cell size and internal coordinates, as well as magnetic moments. Our results show good accordance between calculated and experimental structural and magnetic properties¹⁶ for the studied compounds. Regarding the proposed Ge₂Mn compound, we have fully relaxed the cell size and internal coordinates for four different magnetic configurations, using the nonprimitive 12-atomic cell depicted on Fig. 1. The ground state is found to be ferromagnetic (FM). All the possible deformations of the unit cell (including shear), as well as the relaxation of supercells as big as five unit cells in the [100], [110], or [001] directions with internally broken symmetries have been tested. The system always converges back to the stable FM C16 unit cell. Thus, despite the lack of phonon spectrum calculations,¹⁷ we can safely assume that this compound is at least metastable.

Then, to compare the energetics of the proposed Ge₂Mn compound with the four other Ge–Mn phases, we proceeded with a thermodynamical study based on the grand potential $\Phi_G = E - TS - \sum_i \mu_i N_i$, where E is the energy, T is the temperature of the system, S is the entropy, N is the number of atoms, and μ is the chemical potential. As we apply it, E is the *ab initio* total energy of a cell, the sum is performed over the different species in the cell and TS is zero since *ab initio* calculations are performed at zero temperature. By ignoring the temperature, we do not take into account entropy, which we know has an important role in relative phase stability, typically 15 meV/atom on total energy in a related system.¹⁸ However, size of the four considered unit cells make it particularly difficult to compute phonons in this case, which are needed to evaluate vibrational entropy. Dividing Φ_G by the total number of atoms in the unit cell, we obtain the reduced grand potential $\phi_G^{\text{phase}} = (E_{\text{tot}}/N_{\text{tot}}) - \mu_{\text{Ge}} \cdot C_{\text{Ge}} - \mu_{\text{Mn}} \cdot C_{\text{Mn}}$, where C_{Ge} and C_{Mn} (y in Ge_{1-y}Mn_y) are the concentrations of Ge and Mn, respectively. We now define the relative concentration of species as $C = C_{\text{Ge}} - (1/2) = (1/2) - C_{\text{Mn}}$, and we obtain the following:

$$\phi_G^{\text{phase}} = \frac{E_{\text{tot}}}{N_{\text{tot}}} + \Delta_{\mu} \cdot C - \frac{\mu_{\text{Ge}} + \mu_{\text{Mn}}}{2}, \quad (1)$$

with $\Delta_{\mu} = \mu_{\text{Mn}} - \mu_{\text{Ge}}$ denoting the chemical potential difference between Mn and Ge atoms. By plotting ϕ_G^{phase} versus Δ_{μ} , one gets a straight line for each phase (see Fig. 2), and can then deduce which compound is the most stable depending on the Δ_{μ} in the system. The absolute value of μ_{Mn} and μ_{Ge} is meaningless in this case, since only *ab initio* energy differences matter. Therefore, we choose to shift these values so that the origin of the graph on Fig. 2 is at the intersection of the lines corresponding to the pure Ge and Ge₈Mn₁₁.

One can learn from Fig. 2 that despite the approximations used in these first principle calculations, we find a stability domain for each of the four Ge–Mn known alloys simulated. Thus, the methodology used here describes well

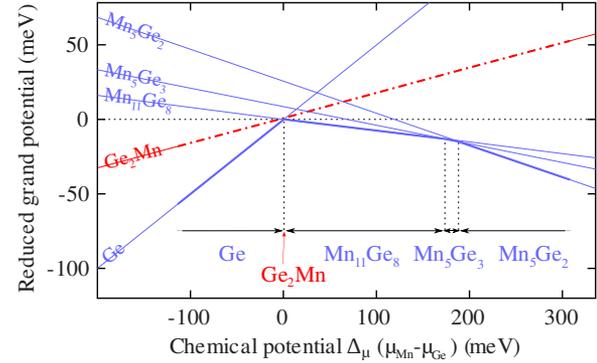


FIG. 2. (Color online) Plot of the reduced grand potential [ϕ_G in Eq. (1)] vs Mn and Ge chemical potential difference (Δ_{μ}) for different Ge–Mn compounds. At a given Δ_{μ} , the thermodynamically stable compound corresponds to the one with the lowest grand potential ϕ_G . Chemical potential and reduced grand potential are arbitrarily put to zero at the frontier of the stability domains of pure Ge and Ge₈Mn₁₁. Continuous lines correspond to the four known compounds, whereas the dotted-dashed line—to Ge₂Mn, which turns out to be not thermodynamically stable.

the energetics of the Ge–Mn system. According to this Ge–Mn phase diagram, the Ge₂Mn compound appears to be thermodynamically unstable (dotted-dashed line in Fig. 2). This is of course expected since it has never been identified experimentally. However, it is worth noticing that the energetic cost of this metastable phase is less than 10 meV/atom (i.e., less than the expected error of the method), which is particularly low. We can thus infer that an out-of-equilibrium growth technique might be able to produce it, in the same way DMS are stabilized [supersaturation of a 2% Ge:Mn solid solution costs more than 20 meV/atom (Ref. 16)].

We will now propose a way to grow the Ge₂Mn compound as a thin film. The obvious issue is to prevent any phase segregation into pure Ge and Ge₈Mn₁₁ or Ge₃Mn₅ clusters, as usually observed. The use of an out-of-equilibrium growth technique like low-temperature MBE would thus be appropriate. The idea is to take advantage of the interfacial and elastic energies, which are of particular importance in a layer-by-layer growth. Indeed, on one hand, Ge₂Mn has a square-based unit cell with a lattice parameter around 6.0 Å (+5.2% as compared to Ge [100], see below), while on the other hand Ge₃Mn₅ and Ge₈Mn₁₁ have hexagonal and orthorhombic symmetries, respectively, with no direct epitaxial relation with Ge. This leads to an interfacial energy of less than 60 meV/Å² in the first case, versus almost 90 meV/Å² in the case of Ge₃Mn₅ [001] on Ge [001],¹⁶ the usually observed configuration.¹⁹ Thus, we can infer that the use of a [100] oriented diamond type substrate with a lattice parameter in the range 5.9–6 Å (e.g., InAs, GaSb, AlSb, and their alloys) will prevent the formation of the two thermodynamically stabler compounds and favor that of Ge₂Mn. The small energy cost would be compensated by the decrease in the interfacial and elastic energies allowed by these *ad hoc* growth conditions. An analogous mechanism is responsible of the favored growth of Ge₃Mn₅ with respect to Ge₈Mn₁₁ in GeMn thin films.^{19,20}

Let us now report on the structural and magnetic properties of the Ge₂Mn as a bulk phase. We find the equilibrium lattice parameters $a = 5.96$ Å and $c = 5.03$ Å, the relaxed internal parameter $x = 0.157$, and the bulk modulus $B = 114$ GPa. The local magnetic moment of Mn atoms is $1.5\mu_B$. We have applied the two-step approach to find the

transition temperature of the compound, as described in Ref. 21. To take into account possible inaccuracy of structural parameters determination, we have calculated the T_C for different lattice sizes and internal parameter x around the computed equilibrium ($\pm 2\%$). The T_C of Ge_2Mn is found to be in the range 200–300 K, depending on the structural parameters used. Moreover, the results show that the application of a biaxial strain along the (a, b) plane can increase the T_C up to 350 K.

We now return to the available experimental data that might give some clues about the possibility to stabilize the proposed Ge_2Mn . Among all the reported experimental synthesis, none of them uses the proposed combination of: layer-by-layer growth technique, Mn concentration and *ad hoc* substrate. First, almost all the previously reported experimental synthesis deal with the growth of DMS alloys with Mn concentration lower than 15%. Second, unsuitable growth techniques such as Mn implantation,⁴ thermal vapor transport,²² supercritical fluid-liquid-solid,²³ etc., are often used. Finally, the substrates used so far are usually Ge, GaAs, or Si, all exhibiting large mismatches with Ge_2Mn (-5.1% , -5.2% , and -8.9% , respectively). In addition, some of the growths were performed on [111]-oriented substrates, thus favoring hexagonal phases like Ge_3Mn_5 .

Only a few experiments involving MBE growth on Ge [100] substrates are relevant for Ge_2Mn stabilization because of the strong phase separation reported,^{6,20,24,25} which leads to Mn-rich regions on one hand, and a nearly pure Ge matrix on the other hand. In the work of Jamet et al.^{6,20} the Mn concentration in the nanocolumns is in the range 30%–40%.²⁰ Depending on the growth conditions, both structural and magnetic properties vary. The nanocolumns seem either fully constrained on the Ge matrix, or appear to relax to some seemingly amorphous structure.²⁰ On the other hand, most nanocolumns have low T_C ,²⁰ while some exhibit ferromagnetism at room temperature.⁶ Transmission electron microscopy images allow us to rule out the clean growth of the Ge_2Mn compound in both fully constrained and amorphous cases, as expected from the strong mismatch (11%) with the diamond Ge along the c -axis (direction of growth). However, the physical properties of the low- T_C nanocolumns²⁰ (30%–40% Mn, T_C of 150–200 K and a local moment of 1.2 μ_B/Mn , and increase in the matrix diamond Ge lattice parameter by 4%) are reminiscent with those computed for the Ge_2Mn compound (33% Mn, T_C of 200–300 K and a local moment of 1.5 μ_B/Mn , and in-plane lattice parameter 5.2% larger than that of diamond Ge). Since the latter growth conditions are not optimal for the bulk stabilization of the Ge_2Mn , the atomic structure inside the nanocolumns would be in a strained and defected form (mainly due to the columnar shape). While the detailed description of this structure is over the scope of the present letter, the reported similarities between the MBE grown samples and the Ge_2Mn support our assumption that such a compound can be stabilized with *ad hoc* MBE growth conditions.

In conclusion, we have shown using DFT calculations coupled with a thermodynamical approach, that a Ge_2Mn compound (Al_2Cu prototype) can be stabilized using *ad hoc* MBE growth conditions. The bulk properties of such a compound are reminiscent with those of the low- T_C nanocolumns, grown in standard MBE conditions.^{6,20} They are also

of great interest for spintronic applications (high Ge content, potentially room temperature ferromagnetism with application of a biaxial strain, compatibility with [100] substrates). Therefore, we think that these predictions deserve future experimental investigations. Furthermore, besides its interesting predicted properties, an analysis of the experimentally observed properties of this compound may become a key step toward full understanding of growth of Ge–Mn nanocolumns and clusters^{6,20,24,25} observed at standard MBE conditions, and thus unraveling the key to high T_C materials design.

The simulations were performed at the CEA supercomputing center (CCRT) and at the Jülich Supercomputing center in the framework of the “High Performance Computing” collaboration between CEA and Helmholtz institutes.

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