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Magnetism of Gd_5Ge_4 from first principles

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The origin of ferromagnetism appearing as a result of a magnetic-field-induced first-order phase transition in Gd_5Ge_4 is explored by calculating the total energy, local exchange splitting, density of states, and magnetic moments. The calculations were performed using the tight-binding linear muffin-tin orbital method within the nonlocal exchange correlation parametrization in the density functional theory including the on-site Coulomb interaction parameter. The total energy as a function of shear distortion along the *a* axis for two different orthorhombic structures is in agreement with experiment, indicating a first-order magnetostructural transition in Gd_5Ge_4. The rearrangement of Gd 5*d* and Ge 4*p* densities of states, the substantial differences in atom-projected band energies, the exchange splitting, and the magnetic moments calculated with ferromagnetic spin arrangements in the orthorhombic Sm_5Ge_4-type and Gd_5Si_4-type structures of Gd_5Ge_4 help to clarify the differences in the magnetic states of these two structures. Our calculations indicate that the Sm_5Ge_4-type structure of Gd_5Ge_4 is the structural ground state and that it is antiferromagnetic.

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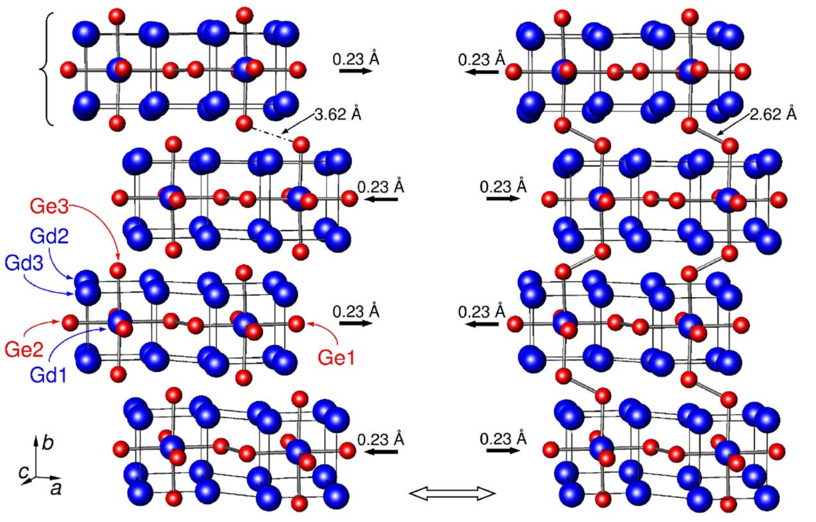
INTRODUCTION

It has been experimentally well established that magnetoelastic effects in gadolinium-based compounds are usually weak, and thus, the Gd-Gd and other interatomic distances rarely change by more than a small fraction of one percent when Gd moments order ferromagnetically (spontaneous magnetostriction) or when a ferromagnetically ordered material is subjected to an external magnetic field (forced magnetostriction).[1] Recent experimental research, however, shows that relatively weak external magnetic fields may trigger sweeping changes in the atomic positions and rearrange chemical bonds, changing some interatomic distances by as much as 30%, resulting in a colossal magnetostriction in self-assembled, nanolayered $Gd_5Si_xGe_{4-x}$ compounds.[2,3] In order to better understand the origin of the remarkable magnetostriction (and also magnetoresistance and magnetocaloric effects) in these materials, all of which are associated with the first-order paramagnetic (PM) to ferromagnetic (FM) or antiferromagnetic (AFM) to FM transitions, we have performed first-principles electronic structure calculations and compared our results with the available experimental data.

The crystallography and basic magnetic properties of the $Gd_5Si_xGe_{4-x}$ compounds were reported by Smith *et al.*[4] and Holtzberg *et al.*[5] in 1967. These materials did not receive much attention until 1997 when Pecharsky and Gschneidner discovered the giant magnetocaloric effect (MCE) in $Gd_5Si_2Ge_2$.[6] Compared to conventional ferromagnets, the enhancement of the MCE in these materials is achieved due to a first-order phase transition when FM ordering is accompanied by a structural transformation.[7,8] Quite importantly, the isothermal entropy change due to the crystal structure change accounts for about a half of the MCE observed in magnetic fields of 2–5 T.[9] Thereafter, magnetostructural transformations at various temperatures became a subject of extensive experimental investigations because of the potential for future applications in near-room-temperature magnetic refrigeration and other energy conversion technologies. In order to better understand the remarkable phenomenology of the $Gd_5Si_xGe_{4-x}$ materials, first-principles theories were applied, resulting in the calculation of the electronic structure and the magnetic, magneto-optical, x-ray magnetic circular dichroism, and giant magnetoresistance properties of $Gd_5Si_2Ge_2$.[10–13] A recent study coupled electronic structure calculations with the mean-field model, leading to reasonable agreement of the theoretically predicted magnetostructural transition temperature and the magnetocaloric effect in $Gd_5Si_2Ge_2$ with experiment.[14] The success of these calculations applied to the rather complex crystal and electronic structure of $Gd_5Si_2Ge_2$ encouraged us to extend our first-principles studies to the other $Gd_5Si_xGe_{4-x}$ compounds.

Experiments indicate that one of the end members of the $Gd_5Si_xGe_{4-x}$ family—namely, the germanide Gd_5Ge_4—is AFM below $T_N \cong 130$ K and it does not exhibit a first-order phase transformation at any temperature down to ∼1.8 K as long as the magnetic field remains below 1 T (Refs. 15 and 16) or the hydrostatic pressure remains below $\sim 10^2$ bar (Ref. 17). Indeed, the electrical resistivity, heat capacity, magnetization, and linear thermal expansion measurements show that a first-order magnetostructural transformation in this compound occurs at atmospheric pressure below 30 K when the external magnetic field exceeds ∼1 T.[8,15,18–22] The x-ray resonant magnetic scattering study of Tan *et al.*[23] con-



(a) Sm_5Ge_4-type (b) Gd_5Si_4-type

FIG. 1. (Color online) The two polymorphic modifications of Gd_5Ge_4: (a) the Sm_5Ge_4-type [O(II)] and (b) the Gd_5Si_4-type [O(I)]. Both are layered structures built from nearly identical pseudo-two-dimensional slabs [one of the slabs is marked by a bracket in (a)] and are related to one another by shear displacements of the neighboring slabs in the directions shown by short arrows near each of the slabs. The numbers above the arrows indicate the magnitude of the displacements. The most drastic difference is observed in Ge3-Ge3 interactions, with corresponding interatomic distances that vary from 3.62 Å in the O(II) to 2.62 Å in the O(I) as indicated in (a) and (b), respectively.

firmed an AFM state as the magnetic ground state of Gd_5Ge_4. Here, the magnetic moments within each nanolayer (slab) are ferromagnetically aligned parallel to the *c* axis, while the coupling between the slabs that are stacked along the *b* direction is antiferromagnetic. *In situ* x-ray powder diffraction experiments carried out isothermally while varying magnetic field[8,16] confirmed that a first-order phase transition occurs in Gd_5Ge_4 between the Sm_5Ge_4-type[4] AFM state and the Gd_5Si_4-type[24] FM state. A recent experimental study by Roy *et al.*[25] indicates that the equilibrium thermodynamic ground state of Gd_5Ge_4 may be, in fact, FM. It is argued that this FM state is avoided due to the kinetic arrest of the first-order O(II) AFM–O(I) FM transition, yet more evidence is needed to determine if the true ground state is AFM or FM. In the vicinity of the first-order phase transition, Gd_5Ge_4 shows complex behavior involving irreversible, partially reversible, and completely reversible magnetic phase changes,[15–21,26–28] apparently fully coupled to crystallographic phase transitions.[8,16] Here, we address some basic issues related to the electronic, magnetic, and structural properties of Gd_5Ge_4 from first-principles electronic structure theory in order to lay a foundation towards understanding the origin of its ferromagnetism, which only occurs as the result of a magnetostructural transition.

CRYSTALLOGRAPHY OF Gd_5Ge_4

The ground-state crystal structure of Gd_5Ge_4 belongs to the orthorhombic (space group symmetry *Pnma*) Sm_5Ge_4-type,[5] also known as O(II)-type,[24] in which Gd atoms occupy the Sm positions and Ge atoms occupy the corresponding Ge sites of the prototype. In this structure, shown in Fig. 1(a), the Gd atoms occupy three different sites (Gd1 in 4*c*, Gd2 and Gd3 in 8*d*). The Ge atoms also occupy three different sites (Ge1 and Ge2 in 4*c*, Ge3 in 8*d*). The O(II)-type structure is built by stacking pseudo-two-dimensional slabs, each formed by five tightly bound monolayers consisting of Gd, Ge, and (Gd+Ge) atoms, along the *b* axis. The slabs are infinite along both the *a* and *c* directions but they are limited to ~7 Å along the *b* direction.

Below ~130 K, Gd_5Ge_4 is AFM in a zero magnetic field, but it can be transformed into the FM state both irreversibly (below 10 K) and reversibly (above 20 K) by magnetic fields exceeding 1 T.[18,26] In the FM state, the Gd_5Ge_4 adopts the Gd_5Si_4-type structure, also known as the O(I)-type structure,[24] which is shown in Fig. 1(b). Therefore, Gd_5Ge_4 may exist in a low-field AFM O(II) and a high-field FM O(I) structure. In the FM state, all the slabs are interconnected via short Ge3-Ge3 bonds ($\delta_{\text{Ge-Ge}}=2.62$ Å, which compares favorably with a 2.45 Å Ge-Ge distance in the elemental Ge adopting the diamond-type structure) but in the AFM state all of these interslab bonds are broken ($\delta_{\text{Ge-Ge}}=3.62$ Å).

During the displacive O(II)↔O(I) transformation structural changes inside the slabs are negligible,[8,16,22] but all of the interslab distances, especially the Ge3-Ge3 bonds, are affected to a much greater degree. A 1.2% volume decrease during the O(II)→O(I) transformation is unusual because typically the phase volume increases upon ferromagnetic ordering, but this relationship between the phase volume is similar to that observed in other $R_5Si_xGe_{4-x}$ compounds.[2,3,29,30] The change in the magnetism from the AFM state in the O(II) allotrope to the FM state in the O(I) polymorph is related to the change of volume and the dramatic change in the interslab Ge3-Ge3 bond lengths.

APPROACH

The local spin density approximation with on-site Coulomb parameter (LSDA+U) approach[31,32] has been employed to investigate the electronic and magnetic properties of the Gd_5Ge_4 system as a function of crystallography. The advantage of this approach over the LSDA and details of its implementation have been discussed in our recent publication;[14] also see references therein. The calculations have been performed using the scalar relativistic version[33] (which includes the mass velocity and Darwin correction terms) of the LSDA+U method implemented in the tight-binding linear muffin-tin orbital[34] (TB-LMTO) scheme with $U=6.7$ eV and $J_0=0.7$ eV.[31] Here, the Langreth-Mehl-Hu[35] parametrization for the exchange correlation functional has been employed because it resulted in estimates that were closer to experimental values for the transition temperatures in the related $Gd_5Si_2Ge_2$ system[14] as compared to the von Barth—Hedin[36] local exchange correlation or the Perdew-Wang[37] nonlocal exchange correlation, which, respectively, somewhat underestimate and overestimate the transition temperature. A total of 125 special k points in the irreducible part of the Brillouin zone were used for k-space integrations.

RESULTS AND DISCUSSION

The x-ray powder diffraction experiments[8,16] show pronounced lattice distortions as the temperature- and/or magnetic-field-induced first-order AFM↔FM transitions in Gd_5Ge_4. For example, when a zero-field-cooled sample is magnetized by a 1.6-T field at any temperature below 7 K and is then heated in this field, the unit-cell volume of the AFM O(II) Gd_5Ge_4 discontinuously decreases by $\Delta V/V = -1.2\%$ while the lattice parameters change by -1.9%, 0.1%, and 0.6% along the a, b, and c axes, respectively, as the increasing temperature triggers the AFM O(II) to FM O(I) transformation around 7 K. When the heating is continued, the reverse FM O(I) to AFM O(II) transformation occurs around 30 K and it is accompanied by changes of the phase volume and unit-cell dimensions that are identical in amplitude but have opposite signs compared to those observed at 7 K. The shear displacements of the slabs along the a direction are accompanied by the largest strain along the a axis. It is this movement of the neighboring slabs in opposite directions along the a axis—i.e., a displacement—which plays a crucial role in altering the electronic structure of the compound and enhancing (or weakening) the interslab exchange coupling. Since the magnetocrystalline anisotropy is small,[38] the same behavior holds for polycrystalline Gd_5Ge_4 as well as for single-crystalline material regardless of the direction of the magnetic field. It should be noted that the Ge-Ge distance between neighboring slabs changes by nearly 30% (Refs. 8 and 16) and the moments are aligned along the b axis in the FM O(I) Gd_5Ge_4 in 1.6-T and higher magnetic fields.[38]

In order to understand the role of shear distortions in the stability of two polymorphic modifications of Gd_5Ge_4, we begin with the O(I)-type structure, which corresponds to a set of relative coordinates $x_i/a=0$ where i is 1,2,…,6, corresponding to six inequivalent atoms in the unit cell. Each of the nonequivalent atoms from one slab is then displaced along the a axis in a negative direction ($x_i/a<0$) against its neighboring slab, which moves by the same $x_i/a>0$ in a positive direction because of symmetry. The total energy was computed assuming the FM ordering of the moments of Gd atoms along the b axis for a series of displacements. The process was repeated for the O(II)-type structure. Both curves are plotted in Fig. 2 with the thick solid line corresponding to minimum energy; the change in the total energy with a shear displacement along the a axis is expressed both in fractional coordinates x_i/a and in the absolute distance. The minimum with the total energy at about −0.30 Å corresponds to the O(II) Gd_5Ge_4 and the minimum with a slightly higher total energy at about −0.08 Å corresponds to the O(I) Gd_5Ge_4. The minimum for the FM O(II) structure is lower by 362 meV/cell than the minimum for the FM O(I) Gd_5Ge_4, which indicates that computationally the FM O(II) structure is more stable ($T=0$ K) than the FM O(I) structure. The clearly distinct minima with an energy barrier between them are consistent with the first-order transformation between the two polymorphs. Even though the computed minima do not precisely coincide with experimental data, the computed shear displacement required to move from one minimum to another (0.22 Å) is in a quantitative agreement with that determined experimentally—i.e., 0.23 Å.[8]

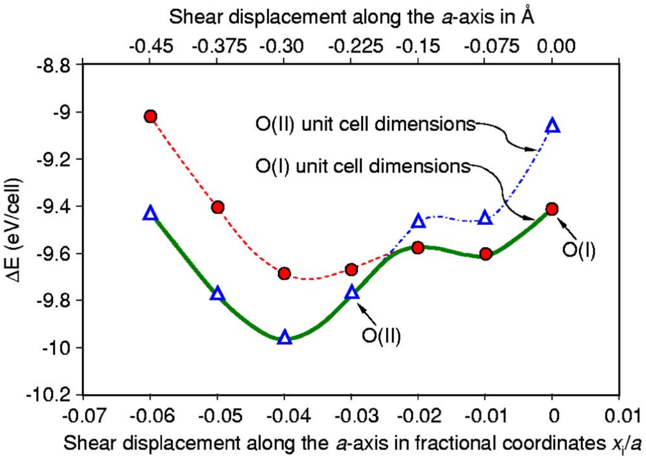


FIG. 2. (Color online) The total energies of the two polymorphic modifications of Gd_5Ge_4, both assuming FM spin arrangements, as functions of shear distortion along the a direction. The total energy minimum around $x_i/a=-0.01$ (−0.08 Å) corresponds to the O(I) FM structure. The total energy minimum at $x_i/a=-0.04$ (−0.30 Å) corresponds to the O(II) FM structure. The arrows point to the total energies computed using experimentally determined (Refs. 8 and 16) crystallographic information for the two polymorphic modifications of Gd_5Ge_4.

Taking into account that the experimentally observed O(II) Gd_5Ge_4 is AFM, the total energy for the AFM spin arrangement between the slabs has also been calculated (not shown in Fig. 2), and it was found to be lower by 52 meV/cell than that for the FM O(II) Gd_5Ge_4, which indicates that the AFM O(II) is the ground-state structure of Gd_5Ge_4. To model both the ferromagnetism of individual slabs and AFM coupling between the slabs, this unusual AFM structure was constructed by doubling the unit cell in the b direction and assigning spin-up configurations to Gd atoms in one slab and spin-down configurations in the neighboring slab. We note that the FM-AFM energy difference is too large for a 1.6-T field to produce a phase change to FM considering the relation $E=-\vec{M}\cdot\vec{B}$; perhaps, it indicates that our computational tools are not so precise for this problem. The total energy difference between the AFM and FM spin arrangements in the neighboring slabs is lower by 63% in the O(II) structure compared to the energy difference between the FM and AFM spin arrangement in the O(I) structure—that is, $[E_{AFM}-E_{FM}]_{O(II)} \cong -0.63[E_{AFM}-E_{FM}]_{O(I)}$. This is

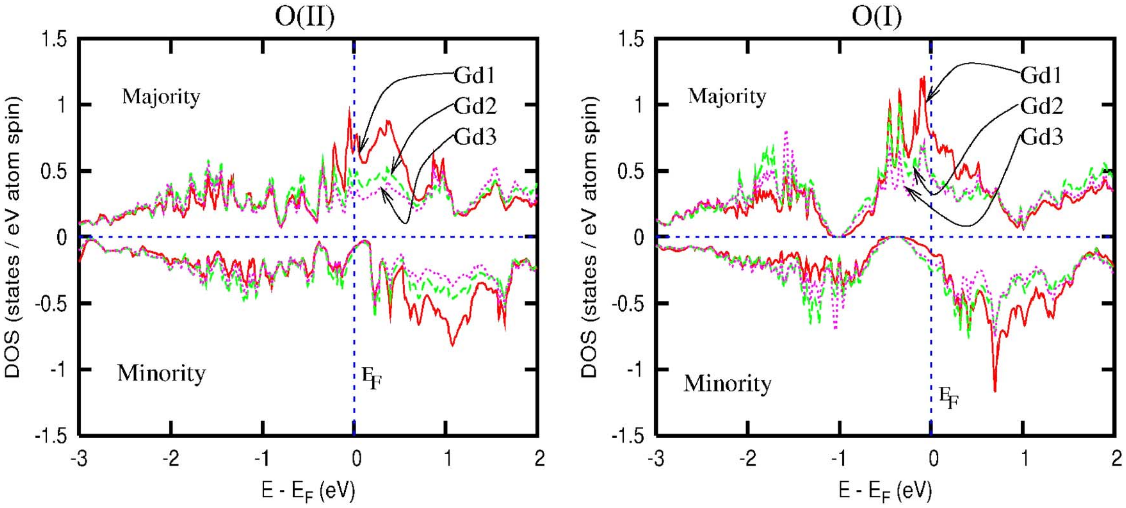


FIG. 3. (Color online) The FM 5d density of state (DOS) of symmetrically inequivalent Gd atoms in the O(II) phase (left) and in the O(I) phase (right).

consistent with the collapse of the FM order in the O(II) Gd_5Ge_4.

Considering the common crystallography of the slabs in Gd_5Ge_4 (Fig. 1), Gd1 is the only symmetrically inequivalent magnetic atom located inside every slab, and therefore, its nearest-neighbor atoms are also from the same slab. The Gd1 atom has six germanium atoms (Ge1, Ge2, and Ge3) and eight gadolinium atoms (Gd2 and Gd3) as its nearest neighbors, and Gd1 of one slab is connected to Gd1 of the neighboring slabs either through the long Ge3-Ge3 pairs in the O(II)-type or through the short Ge3-Ge3 pairs in the O(I) Gd_5Ge_4; see Fig. 1. As indicated in the previous paragraph, the interactions between Gd1 atoms belonging to neighboring slabs through the short Ge3-Ge3 pairs with the strong Ge-Ge bonding result in a ferromagnetic ground state, while the same interactions through the long Ge3-Ge3 pairs with much weaker Ge-Ge bonding result in the antiferromagnetic ground state. The dramatic difference in the hybridization between 5d electrons of Gd1 and 4p electrons of Ge3 depends on whether the short Ge3-Ge3 pairs [as in the O(I) structure] or the long Ge3-Ge3 pairs [as in the O(II) structure] are formed and is primarily responsible for the difference in the interslab coupling in the O(I) and O(II) structures; see next paragraph. A similar connectivity (Gd1-Ge2-Ge1-Gd1), which, however, remains unaffected by the same structural perturbation, is found inside every slab. The difference in band energies between Gd1 and its nearest-neighboring Gd atoms considering FM order shows how they interact with each other when the neighboring slabs interact via short and long Ge3-Ge3 bonds. The atom projected band energy can be defined in terms of atom projected density of states [$D^i(E)$] and is given as

$$E_b^i = \int_{-\infty}^{E_F} ED^i(E)dE.$$

In the O(II) Gd_5Ge_4, the difference in band energies between Gd1 and Gd2 is +158 meV and between Gd1 and Gd3 it is −992 meV. They change to +893 meV and +393 meV, respectively, in the O(I) Gd_5Ge_4. This variation of band energies indicates that the change in the Ge3-Ge3 bonding together with the phase volume change greatly affects the relative band energies of the neighboring Gd atoms in the O(I) and O(II) allotropes of Gd_5Ge_4 respectively.

Within the LSDA+U-based TB-LMTO with atomic sphere approximation (ASA) theory, the local exchange splitting can be evaluated as a difference of the respective potential parameters (C) at the center of the atom projected bands. The calculated 5d local exchange splittings for Gd1, Gd2, and Gd3 of the FM O(I) Gd_5Ge_4 are 1.58 eV, 1.37 eV, and 1.32 eV, respectively, which are higher than the corresponding values 1.25 eV, 1.13 eV, and 1.17 eV in the FM O(II) Gd_5Ge_4. Assuming the FM states, in which all Gd moments are oriented along the b direction, this local splitting causes an exchange splitting in the majority- and minority-spin bands, giving rise to the 5d magnetic moments of Gd atoms. The calculated magnetic moments for Gd1, Gd2, and Gd3 of the FM O(I) Gd_5Ge_4 are $7.62\mu_B$, $7.50\mu_B$, and $7.39\mu_B$ respectively, all of which are higher than the corresponding values of $7.36\mu_B$, $7.24\mu_B$, and $7.19\mu_B$ in the FM O(II) Gd_5Ge_4. The decrease in the magnetic moments of 5d electrons (the contribution from the Gd 4f electrons is fixed at $7\mu_B$) from the FM O(I) to the FM O(II) is 42% for Gd1, 52% for Gd2, and 51% for Gd3, indicating a substantial weakening of the magnetic interactions in the O(II) Gd_5Ge_4. The magnetic moments calculated with the AFM spin alignment in the O(II) Gd_5Ge_4 are slightly lower—i.e., $7.29\mu_B$, $7.16\mu_B$, and $7.19\mu_B$ for Gd1, Gd2, and Gd3, respectively, which is a 53%, 68%, and 51% reduction in the magnetic moments of 5d electrons compared to the FM O(I). These changes in the magnetic moments are consistent with the 63% decrease of exchange coupling energy noted above.

In order to probe how the structural change affects the electronic structure and magnetism of Gd_5Ge_4, the 5d Gd and 4p Ge DOS were calculated with the FM order imposed in both the O(I) and O(II) structures. Figure 3 shows that the 5d DOS of symmetrically inequivalent Gd atoms in the O(I)

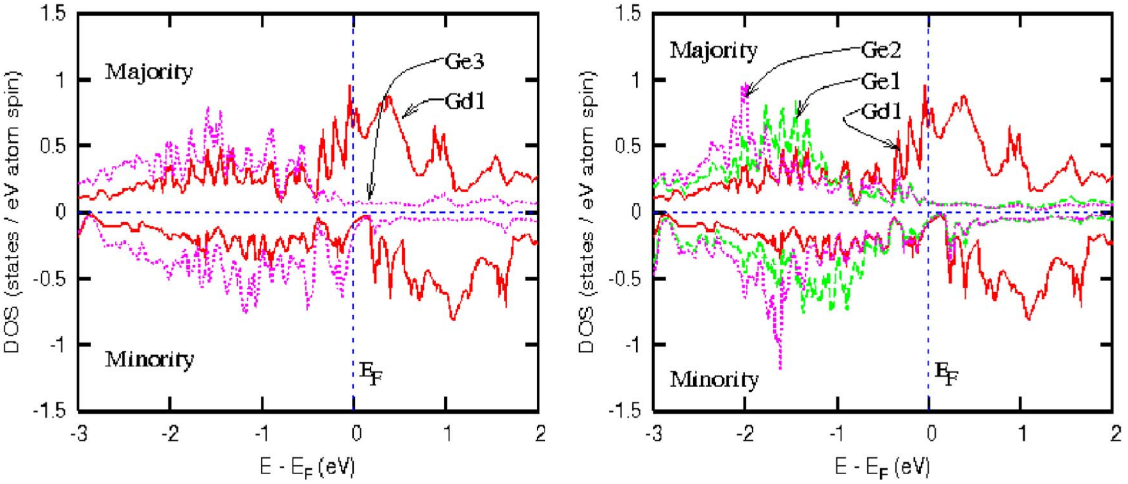


FIG. 4. (Color online) (Left) The FM O(II) phase 5*d* DOS of Gd1 and 4*p* DOS of Ge3. The spin-down 4*p* DOS of Ge3 is larger at the Fermi level than spin-down 5*d* DOS of Gd1. (Right) The FM 5*d* DOS of Gd1 and 4*p* DOS of Ge1 and Ge2. The spin-down 4*p* DOS of Ge1 and Ge2 are almost same with the spin-down 5*d* DOS of Gd1 at the Fermi level.

and O(II) Gd_5Ge_4 are different at the Fermi level. The 5*d* DOS and band splitting at the Fermi level for the O(I) structure are higher than for the O(II) structure, resulting in higher 5*d* magnetic moments. Figure 4 shows that the spin-down 4*p* DOS of Ge3 is larger at and below the Fermi level compared to the spin-down 5*d* DOS of Gd1 within the O(II) structure, indicating 30% 5*d* Gd1 and 70% 4*p* Ge3 hybridization in the same band. These spin-down 4*p* states have been pushed towards the Fermi level because of the weak Ge3-Ge3 bonding, and they have significant 5*d* character in the O(II) structure, resulting in a reduced magnetic moment on the Gd atoms surrounding Ge3 sites. On the other hand, the spin-down 4*p* DOS of Ge1 and Ge2 and the spin-down 5*d* DOS of Gd1 are nearly identical at the Fermi level, indicating 50% 5*d* Gd1 and 50% 4*p* Ge1/Ge2 hybridization in the same band. In contrast to this, the spin-down 5*d* Gd1 states are hybridized nearly equally with the 4*p* states of all Ge atoms in the O(I) Gd_5Ge_4, regardless whether these are interslab Ge3 or intraslab Ge1 and Ge2 4*p* states as seen in Fig. 5. Similarity in the spin-down Ge 4*p* Gd1 5*d* hybridization in the O(I) Gd_5Ge_4 and the hybridization differences observed in the O(II) Gd_5Ge_4 are consistent with the similarities and differences in the Gd-Ge-Ge-Gd bonding and magnetism in the two allotropic modifications of Gd_5Ge_4.

CONCLUSIONS

In summary, the total energy calculations reveal that the Sm_5Ge_4-type [O(II)] Gd_5Ge_4 has an antiferromagnetic ground state and a lower energy than the ferromagnetic Gd_5Si_4-type [O(I)] Gd_5Ge_4 in agreement with experiment. The total energy versus shear perturbation behavior shows a first-order phase transformation between FM O(II) Gd_5Ge_4 and FM O(I) Gd_5Ge_4. The interslab exchange coupling energy in the O(II) Gd_5Ge_4 is lower than that of the O(I) Gd_5Ge_4. The band energy analysis indicates that Gd atoms in O(II) Gd_5Ge_4 and O(I) Gd_5Ge_4 are bonded differently in association with the difference in the interslab Ge3-Ge3 bond-

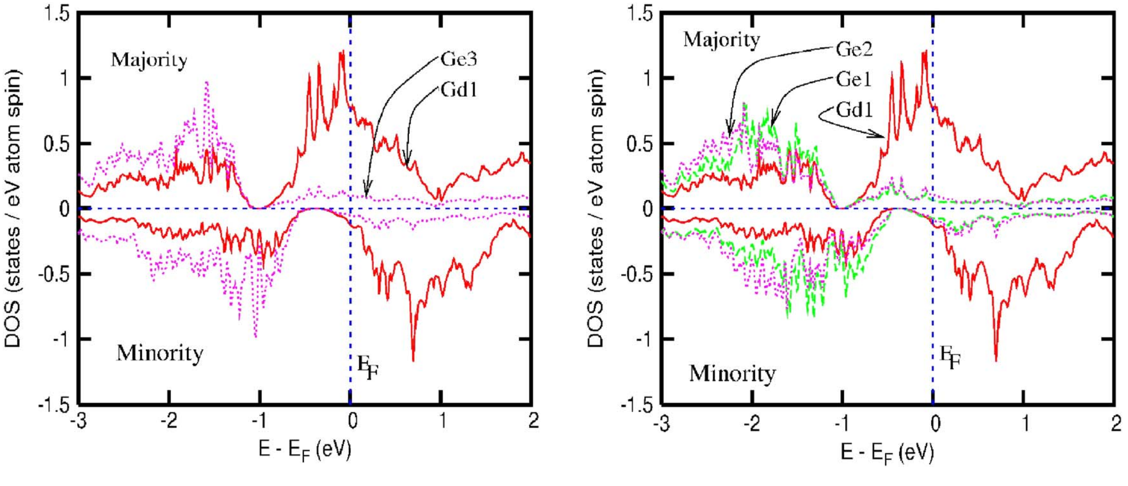


FIG. 5. (Color online) (Left) The FM O(I) phase 5*d* DOS of Gd1 and 4*p* DOS of Ge3 and (Right) the FM 5*d* DOS of Gd1 and 4*p* DOS of Ge1 and Ge2.

ing. The FM 5*d* local exchange splitting of the Gd atoms in O(I) Gd_5Ge_4 is larger than in the O(II) Gd_5Ge_4. There is a substantial difference (of the order of 50%) in the 5*d* magnetic moments of Gd atoms in the O(II) and O(I) Gd_5Ge_4 phases. The 5*d* DOS of Gd atoms and 4*p* DOS of Ge3 atoms are completely different in the O(II) and O(I) structures.

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