Electronically Induced Ferromagnetic Transitions in Sm5Ge4-Type Magnetoresponsive Phases

Jinlei Yao
*Suzhou University of Science and Technology*

Yuemei Zhang
*Iowa State University*

Peng L. Wang
*McMaster University*

Laura Lutz-Kappelman
*Iowa State University, lclutz@iastate.edu*

Gordon J. Miller
*Iowa State University, gmiller@iastate.edu*

Follow this and additional works at: [http://lib.dr.iastate.edu/chem_pubs](http://lib.dr.iastate.edu/chem_pubs)

Part of the [Materials Chemistry Commons](http://lib.dr.iastate.edu/chem_pubs), [Other Chemistry Commons](http://lib.dr.iastate.edu/chem_pubs), [Other Materials Science and Engineering Commons](http://lib.dr.iastate.edu/chem_pubs), and the [Physical Chemistry Commons](http://lib.dr.iastate.edu/chem_pubs)

The complete bibliographic information for this item can be found at [http://lib.dr.iastate.edu/chem_pubs/660](http://lib.dr.iastate.edu/chem_pubs/660). For information on how to cite this item, please visit [http://lib.dr.iastate.edu/howtocite.html](http://lib.dr.iastate.edu/howtocite.html).

---

This Article is brought to you for free and open access by the Chemistry at Iowa State University Digital Repository. It has been accepted for inclusion in Chemistry Publications by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Electronically Induced Ferromagnetic Transitions in Sm5Ge4-Type Magnetoresponsive Phases

Abstract
The correlation between magnetic and structural transitions in Gd5SixGe4−x hampers the studies of valence electron concentration (VEC) effects on magnetism. Such studies require decoupling of the VEC-driven changes in the magnetic behavior and crystal structure. The designed compounds, Gd5GaSb3 and Gd5GaBi3, adopt the same Sm5Ge4-type structure as Gd5Ge4 while the VEC increases from 31 e−/formula in Gd5Ge4 to 33 e−/formula in Gd5GaPn3 (Pn: pnictide atoms). As a result, the antiferromagnetic ground state in Gd5Ge4 is tuned into the ferromagnetic one in Gd5GaPn3. First-principles calculations reveal that the nature of interslab magnetic interactions is changed by introducing extra p electrons into the conduction band, forming a ferromagnetic bridge between the adjacent [≈2Gd5T4] slabs.

Disciplines
Materials Chemistry | Other Chemistry | Other Materials Science and Engineering | Physical Chemistry

Comments

Authors
Jinlei Yao, Yuemei Zhang, Peng L. Wang, Laura Lutz-Kappelman, Gordon J. Miller, and Yurij Mozharivskyj

This article is available at Iowa State University Digital Repository: http://lib.dr.iastate.edu/chem_pubs/660
Electronically Induced Ferromagnetic Transitions in Sm$_5$Ge$_4$-Type Magnetoresponsive Phases

Jinlei Yao,$^{1,2}$ Yuemei Zhang,$^3$ Peng L. Wang,$^2$ Laura Lutz,$^3$ Gordon J. Miller,$^3$ and Yurij Mozharivskyj$^{2,*}$

$^1$Research Center for Solid State Physics and Materials, School of Mathematics and Physics, Soochow University of Science and Technology, Suzhou 215009, China
$^2$Department of Chemistry and Chemical Biology, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4M1, Canada
$^3$Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA

(Received 3 October 2012; published 15 February 2013)

The correlation between magnetic and structural transitions in Gd$_5$Si$_{1-x}$Ge$_x$ hampers the studies of valence electron concentration (VEC) effects on magnetism. Such studies require decoupling of the VEC-driven changes in the magnetic behavior and crystal structure. The designed compounds, Gd$_5$GaSb$_3$ and Gd$_5$GaBi$_3$, adopt the same Sm$_3$Ge$_4$-type structure as Gd$_5$Ge$_4$ while the VEC increases from 31 e$^-$/formula in Gd$_5$Ge$_4$ to 33 e$^-$/formula in Gd$_5$GaPn$_3$ (Pn: pnictide atoms). As a result, the antiferromagnetic ground state in Gd$_5$Ge$_4$ is tuned into the ferromagnetic one in Gd$_5$GaPn$_3$. First-principles calculations reveal that the nature of inter slab magnetic interactions is changed by introducing extra p electrons into the conduction band, forming a ferromagnetic bridge between the adjacent f$_{12}$Gd$_{T_4}$ slabs.

DOF: 10.1103/PhysRevLett.110.077204 PACS numbers: 75.30.Sg, 61.50.Ks, 64.70.kd, 75.30.Kz

Magnetic materials with first-order magnetostuctural transitions are of both fundamental and technological interest due to a strong correlation between structural, electronic, and magnetic degrees of freedom and the concomitantly emergent properties, such as magnetic-field-induced shape memory effect, giant magnetoresistance, and magnetocaloric effects [1–5]. These properties originate from the energetic, magnetic and structural transitions in response to an external magnetic field. Therefore, understanding and manipulation of the magnetic interactions and crystal structures play an essential role in utilizing these effects for potential applications, e.g., solid-state magnetic refrigeration, magnetic actuators, and sensors. Rare-earth intermetallics of the form Sm$_3$Ge$_4$ are a unique system which shows a first-order magnetic-martensitic transition accompanied by a giant magnetocaloric effect near room temperature [2,6,7].

The magnetic-martensitic transition in Gd$_5$Ge$_4$ is featured by a collective shear movement of $\frac{7}{2}$[Gd$_{T_4}$] slabs (T: Si, Ge or another p element), which constructs the three related structures through different inter slab T-T bonds in this system: (i) broken dimers in the orthorhombic Sm$_3$Ge$_4$-type structure (space group Pnma); (ii) both broken and intact dimers in the monoclinic Gd$_5$Si$_2$Ge$_2$ structure ($P11_2_1/a$); and (iii) intact ones in the other orthorhombic Gd$_5$Si$_4$ structure (Pnma) [6,8]. The ground state of Gd$_5$Si$_4$-type phases is ferromagnetic (FM) whereas the Sm$_3$Ge$_4$ phases are antiferromagnetic (AFM) [6,7,9,10]. It was successfully demonstrated that valence electron concentration (VEC) is a practicable approach to tune the structural or magnetostuctural transitions in Gd$_5$Si$_{1-x}$Ge$_x$ and related R$_5$T$_4$ (R: rare earth) systems, e.g., Gd$_5$Ga$_x$Ge$_{4-x}$ [11], Gd$_5$Si$_{4-x}$P$_x$ [12], (La/Ce)$_5$-xC$_x$Ge$_4$ [13], R$_{5-x}$M$_x$Ge$_4$ [14], Yb$_5$Li$_3$Ge$_4$ [15], and Gd$_{5-x}$Eu$_x$Ge$_4$ [16]. However, the strong coupling between the magnetic and structural transitions presents a challenge to studying the VEC effects on magnetic interactions. To investigate this effect on magnetism of Gd$_5$Si$_{1-x}$Ge$_x$, we first need to decouple magnetic and structural transitions due to the VEC.

It is well established that the magnetic transitions in Gd$_5$Si$_{1-x}$Ge$_x$ correlate with the formation or cleavage of the inter slab T-T dimers, which strongly affect the magnetic exchange interactions between the FM $\frac{7}{2}$[Gd$_{T_4}$] slabs and, thus, the global magnetic alignment [8,9]. For example, in Gd$_5$Ge$_4$, the ambient AFM order is converted to the FM state under hydrostatic pressure, accompanied by a structural transformation from the Sm$_3$Ge$_4$ type (with broken inter slab T-T dimers) to the Gd$_5$Si$_4$ type (with intact dimers) [route 1 in Fig. 1] [17]. The transformation can be seen as an internal oxidation process, $2\text{Ge}^{4-} \rightarrow \text{Ge}_2^{6-} + 2e^-$, namely, two inter slab Ge$^{4-}$ monomers forming a covalent Ge-Ge bond and releasing two electrons. These two electrons enter the conduction band to tune the Gd-Gd magnetic coupling via the Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions, resulting in an AFM-FM transition. It should be noted that this route involves the structural transition, too.

According to the Zintl-Klemm concept [6,8,11], the Sm$_3$Ge$_4$ and Gd$_5$Si$_4$-type Gd$_5$Ge$_4$ compounds can be written as $(\text{Gd}^{3+})_3(\text{Ge}^{6+})_2(\text{Ge}^{4-})_2(1e^-)$ and $(\text{Gd}^{3+})_5 \times (\text{Ge}^{6+})_2(3e^-)$, respectively, considering that intact T-T dimers exist within the slabs of both structures. Is there another way to adjust the VEC to the same conduction electron number and thus to induce FM order without a structural transition? A suggested pathway (route 2) is shown in Fig. 1. While maintaining the Sm$_3$Ge$_4$ structure, the VEC changes from 31 to 33 e$^-$/formula unit (f.u.)
by replacing two tetravalent Ge atoms with two pentavalent pnictide (Pn) ones, in order to obtain the same conduction electron count as in the Gd₅Si₄-type Gd₅Ge₄ compound (3 e⁻/f.u.). Route 2 leads to a hypothetical “(Gdğı⁺₃)(Ge₅⁻)(Pnʰ⁻)(Pnⁿ⁻)(3e⁻)” phase isostructural with Sm₅Ge₄, which is expected to show FM interactions through tuning the VEC.

To verify this idea (route 2), we first study the magnetic ground state and magnetic interactions through ab initio calculations on the Sm₅Ge₂-type phases, Gd₅Ge₄, and “Gd₅Ge₂Sb₂”, with the latter having Sb atoms on the interslab T₁ sites [Fig. 1]. To avoid involving any distance effect on magnetic interactions, the calculations used the same set of crystal data for Gd₅Ge₄ and Gd₅Ge₂Sb₂, i.e., the crystal data of Gd₅Ge₄ at 6.1 K and in the absence of a magnetic field [9]. Sb prefers the interslab T₁ site over the intraslab T₂/T₃ sites, due to its larger atomic size and one more valence electron than Ge [18,19]. The FM/AFM models were assigned the parallel/antiparallel spin alignment between the neighboring FM \( \frac{3}{2}[\text{Gd₅T}_3] \) slabs.

The first-principles calculations were carried out using the projector augmented wave method [20,21] coded in the Vienna ab initio simulation package (VASP) [22,23] with the plane wave cutoff energy of 500 eV, and a set of \( 6 \times 3 \times 6 \) \( k \) points for the irreducible Brillouin zone. Exchange and correlation were treated by the generalized gradient approximation [24].

To describe the electron correlation associated with the Gd 4f states, on-site repulsion was applied using the LSDA + U method [25]. The well-known Hubbard and exchange parameters of \( U = 6.7 \) eV and \( J = 0.7 \) eV for Gd 4f states were employed in the calculations [26].

The calculations confirm the AFM ground state of Gd₅Ge₄ [Table I] in agreement with prior experimental and theoretical investigations [9,10]. In the FM state of Gd₅Ge₄ [Fig. 2], the spin-down density of states (DOS) of Ge at T₁ at and just below the Fermi level \( (E_F) \) is higher than the spin-up counterpart. These Ge 4p states strongly hybridize with the Gd 5d states, which accommodates a large number of conduction electrons in the spin-down direction. Accordingly, the \( E_F \) resides in a large valley in the magnetic moment of spin-polarized conduction electrons, whose value is derived from the difference of integrated DOS between the spin-up and spin-down channels, subtracting the Gd 4f moment fixed at \( 7 \mu_B \).

Interestingly, a pseudogap is situated just above \( E_F (~0.2 \) eV) in the spin-down DOS [Fig. 2]. As the VEC increases from 31 to 33 e⁻/f.u., and thus \( E_F \) is lifted above the pseudo-gap, a number of conduction electrons will be confined in the spin-up channel. As a result, the conduction-electron magnetic moment, mainly from the Gd 5d electrons, will be significantly enhanced [Fig. 2], leading to an AFM-FM transition. This VEC-tuned magnetic transition is confirmed in the calculations of Gd₅Ge₂Sb₂ with VEC = 33 e⁻/f.u. In Fig. 2, one can clearly see that the \( E_F \) located just above the band gap in the spin-down channel and Gd 5d spin-up and spin-down states display a large exchange splitting, increasing the spin polarization of the conduction electrons. On average, the Gd 5d moment is almost doubled, from 0.18 \( \mu_B \) in Gd₅Ge₄ to 0.36 \( \mu_B \) in Gd₅Ge₂Sb₂, suggesting a substantial enhancement of the FM interactions due to the VEC that stabilizes the FM ground state with an energy 0.592 eV/cell lower than that of the AFM state [Table I].

To validate the theoretical prediction of the AFM-FM transition tuned by the VEC in the Sm₅Ge₂-type phases without a structural transition, a Gd₅Ge₂Sb₂ sample with

![FIG. 1 (color online). Schematic diagram of the magnetostructural transition between the Sm₅Ge₂- and Gd₅Si₄-type structures (route 1), and of the magnetic transition in the Sm₅Ge₄-type phase (route 2). Pn: pnictide elements.](image-url)
VEC = 33 e⁻/f.u. was synthesized. The experimental details are described in Supplemental Material (SM) [27]. Gd₅Ge₂Sb₂, however, adopts the Eu₅Au₄ structure (Cmca) [Tables S1 and S2 in SM], rather than the desired Sm₅Ge₄ structure, in agreement with the previous reports [18,19]. In order to obtain the desired structure and VEC, the designed composition was adjusted to Gd₅GaSb₃ and Gd₅GaBi₃. The single-crystal and powder x-ray diffraction studies show that both compounds adopt the Sm₅Ge₄ structure with broken interslab T₁–T₃ dimers of 3.942(1) and 4.021(1) Å for the respective Sb and Bi compounds [Table S1 and Fig. S1 in SM]. Crystallographic analysis reveals that the Ga and Pn atoms share the intraslab T₂=T₃ sites, whereas the interslab T₁ site is exclusively occupied by the Pn elements [Table S2 in SM].

As predicted by the calculations, the VEC increase has an enormous effect on the magnetic properties. Isothermal magnetization measurements [Fig. 3(a)] reveal that the ground state of Gd₅Ge₄ is AFM and an AFM-FM transition couples with a Sm₅Ge₄ – Gd₅Si₄ structural transformation occurring around 18 kOe at 5 K, in agreement with the previous studies [9]. In contrast, Gd₅GaSb₃ and Gd₅GaBi₃ display a typical FM behavior and saturated magnetic moments of 7.01 and 7.03 μB/Gd, respectively, which are close to the theoretical moment of 7 μB (4f'). Moreover, the temperature-dependent magnetization curves in Fig. 3(b) show that Gd₅Ge₄ remains in the AFM state in a low magnetic field, whereas Gd₅GaPn₃ retain the FM state up to the Curie temperatures, T_C = 222 and 208 K for the Sb and Bi samples, respectively. The magnetization of Gd₅GaPn₃ measured during heating and cooling in the magnetic fields of 0.1 and 10 kOe does not show a temperature hysteresis around T_C [Fig. S2 in SM], indicating absence of structural transitions in the vicinity of the magnetic ones. These comparative studies suggest that the VEC increase from 31 to 33 e⁻/f.u. promotes transformation of the AFM ground state in Gd₅Ge₄ into the FM one in Gd₅GaPn₃.

The collective magnetic behaviors of rare-earth-main-group materials, including Gd₅Si₅Ge₄ – Gd₅Si₄, are believed to be controlled by RKKY interactions between the local rare-earth magnetic moments [6–8,10]. It is generally accepted that RKKY interactions can be tuned by varying the interatomic distance or conduction electron concentration. Previous studies of Gd₅Ge₄ have mostly focused on the distance effect and consequent metamagnetic transitions through chemical (substitution of smaller Si for Ge) or hydrostatic pressure [17,28].

In this work, the distance-mediated RKKY interactions are not likely to play a crucial role, considering the following facts. First, the above calculations for Gd₅Ge₂Sb₂ use the crystallographic data identical to Gd₅Ge₄, i.e., the same Gd-Gd distances, but shift the ground state from AFM to FM. The first-principles calculations for Gd₅GaSb₃ using experimental crystallographic data yield band characteristics similar to those of Gd₅Ge₂Sb₂ [Fig. 2]—e.g.,
FIG. 4. Exchange interaction, $J_{\text{RKKY}}$, as a function of the conduction-electron number per formula in the Sm$_5$Ge$_4$-type Gd$_5$Ge$_4$ compound. $J_{\text{RKKY}}$ is estimated based on the RKKY model using a nearly free electron approximation. $J_{\text{RKKY}}$ of short (3.53 Å) and long (4.07 Å) interslab Gd-Gd bonds is presented in the figure. Values for $J_{\text{RKKY}}$ are normalized to equal $-1$ for 3.53 Å and 0.8 $e^{-}$/formula.

conduction electron confinement in the spin-up states, due to the presence of a band gap just below $E_F$ ($-0.05 \sim -0.30$ eV) in the spin-down DOS, and enhanced Gd 5d moments at $E_F$—resulting in a FM ground state [Table I]. Second, in Sm$_5$Ge$_4$-type phases, the interslab Gd-Gd distance can support AFM interactions up to 5 Å [8]. However, the bonds in Gd$_5$GaP$_n$ extend only up to 4.4 Å [Table S3 in SM], still within the AFM range. Third, recent experiments on Gd$_5$Ge$_4$-P$_n$ and Gd$_5$Ge$_4$-Sb$_n$ show that both systems are of the FM Sm$_5$Ge$_4$ type, regardless of size effects arising from the substitution of smaller or larger P/Sb for Ge [18,19,29].

Now, we consider the RKKY interactions from the perspective of spin polarized conduction electrons. Within the nearly free-electron model, the RKKY exchange interaction, $J_{\text{RKKY}}$, is given by $J_{\text{RKKY}} \propto F(2k_FR)$ with $F(x) = (x \cos x - \sin x)/x^2$ and $R$ being an interatomic distance [30]. The Fermi wave vector ($k_F$) of the free-electron gas is related to the conduction-electron number ($N_e$) by $k_F = (3\pi^2 N_e/V)^{1/3}$, in which $V$ is the unit-cell volume. For the Sm$_5$Ge$_4$-type Gd$_5$Ge$_4$ compound, $N_e$ is 1 $e^{-}$/f.u. (≈ 4 $e^{-}$/cell) in the conduction band and its $J_{\text{RKKY}}$ is estimated to be negative, i.e., AFM, for both the short (3.53 Å) and long (4.07 Å) interslab Gd-Gd bonds [Fig. 4]. One can see that $J_{\text{RKKY}}$ and hence magnetic coupling change sign with an increasing electron concentration. At $N_e = 3$ $e^{-}$/f.u., corresponding to the (Gd$^{3+}$)$_5$(Ga, Pn)$^{6-}$ (Pn$^{3-}$)$_2$(3e$^-$) formula isoelectronic with Gd$_5$Si$_4$, the RKKY interactions are FM. The effective interslab exchange, $J_0$, can be estimated from the total energy difference between AFM and FM configurations. $J_0 = -0.200$ eV/cell for Gd$_5$Ge$_4$ changes to 0.422 eV/cell for Gd$_5$GaSb$_3$, indicating a transition from an AFM to FM magnetic coupling. Since the RKKY interactions are influenced by the conduction electrons, the Pn substitution introduces extra $p$ electrons into the conduction band to enhance the magnetic exchange interactions, thus promoting the onset of the interslab FM coupling.

In summary, we have demonstrated that VEC is particularly important in establishing FM interactions in Sm$_5$Ge$_4$-type phases. Interslab AFM coupling of Gd$_5$Ge$_4$ can be transformed into the FM type by substitution of electron-richer atoms. We believe that the VEC can be used as a powerful chemical approach to finely tailor the magnetic properties of other rare-earth intermetallics. Importantly, the magnetoresponsive effects in low magnetic fields for first-order magnetostructural materials can be optimized through tuning their VEC.

This work was supported by a Discovery Grant from the Natural Sciences and Engineering Research Council of Canada and by a grant from the ACS Petroleum Research Fund.

*Corresponding author.
mozhar@mcmaster.ca
