

2013

Electronically Induced Ferromagnetic Transitions in Sm₅Ge₄-Type Magnetoresponse 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, llutz@iastate.edu

Gordon J. Miller

Iowa State University, gmiller@iastate.edu

Follow this and additional works at: http://lib.dr.iastate.edu/chem_pubs

 Part of the [Materials Chemistry Commons](#), [Other Chemistry Commons](#), [Other Materials Science and Engineering Commons](#), and the [Physical Chemistry Commons](#)

The complete bibliographic information for this item can be found at 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>.

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 Magneto-responsive Phases

Abstract

The correlation between magnetic and structural transitions in Gd₅SixGe_{4-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

This article is from *Physical Review Letters* 110 (2013): 1, doi:10.1103/PhysRevLett.110.077204. Posted with permission.

Authors

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

Electronically Induced Ferromagnetic Transitions in Sm_5Ge_4 -Type Magnetoresponse Phases

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

¹Research Center for Solid State Physics and Materials, School of Mathematics and Physics, Suzhou University of Science and Technology, Suzhou 215009, China

²Department of Chemistry and Chemical Biology, McMaster University, 1280 Main Street West, Hamilton, Ontario L8S 4M1, Canada

³Department 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 $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$ 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_5GaSb_3 and Gd_5GaBi_3 , adopt the same Sm_5Ge_4 -type structure as Gd_5Ge_4 while the VEC increases from $31 e^-/\text{formula}$ in Gd_5Ge_4 to $33 e^-/\text{formula}$ in Gd_5GaPn_3 (Pn: pnictide atoms). As a result, the antiferromagnetic ground state in Gd_5Ge_4 is tuned into the ferromagnetic one in Gd_5GaPn_3 . 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 $\frac{1}{2}[\text{Gd}_5\text{T}_4]$ slabs.

DOI: [10.1103/PhysRevLett.110.077204](https://doi.org/10.1103/PhysRevLett.110.077204)

PACS numbers: 75.30.Sg, 61.50.Ks, 64.70.kd, 75.30.Kz

Magnetic materials with first-order magnetostructural 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 synergetic 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 $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$ are a unique system which shows a first-order magnetic-martensitic transformation accompanied by a giant magnetocaloric effect near room temperature [2,6,7].

The magnetic-martensitic transition in $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$ features a collective shear movement of $\frac{1}{2}[\text{Gd}_5\text{T}_4]$ slabs (T : Si, Ge or another p element), which construct the three related structures through different interslab T - T bonds in this system: (i) broken dimers in the orthorhombic Sm_5Ge_4 -type structure (space group $Pnma$); (ii) both broken and intact dimers in the monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ structure ($P112_1/a$); and (iii) intact ones in the other orthorhombic Gd_5Si_4 structure ($Pnma$) [6,8]. The ground state of Gd_5Si_4 -type phases is ferromagnetic (FM) whereas the Sm_5Ge_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 magnetostructural transitions in $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$ and related $R_5\text{T}_4$ (R : rare earth) systems, e.g., $\text{Gd}_5\text{Ga}_x\text{Ge}_{4-x}$ [11], $\text{Gd}_5\text{Si}_{4-x}\text{P}_x$ [12], $(\text{La/Ce})_{5-x}\text{Ca}_x\text{Ge}_4$ [13], $R_{5-x}\text{Mg}_x\text{Ge}_4$ [14], Yb_4LiGe_4

[15], and $\text{Gd}_{5-x}\text{Eu}_x\text{Ge}_4$ [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 $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$, we first need to decouple magnetic and structural transitions due to the VEC.

It is well established that the magnetic transitions in $\text{Gd}_5\text{Si}_x\text{Ge}_{4-x}$ correlate with the formation or cleavage of the interslab T - T dimers, which strongly affect the magnetic exchange interactions between the FM $\frac{1}{2}[\text{Gd}_5\text{T}_4]$ slabs and, thus, the global magnetic alignment [8,9]. For example, in Gd_5Ge_4 , the ambient AFM order is converted to the FM state under hydrostatic pressure, accompanied by a structural transformation from the Sm_5Ge_4 type (with broken interslab T - T dimers) to the Gd_5Si_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 interslab 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_5Ge_4 - and Gd_5Si_4 -type Gd_5Ge_4 compounds can be written as $(\text{Gd}^{3+})_5(\text{Ge}_2^{6-})(\text{Ge}^{4-})_2(1e^-)$ and $(\text{Gd}^{3+})_5 \times (\text{Ge}_2^{6-})_2(3e^-)$, 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_5Ge_4 structure, the VEC changes from 31 to $33 e^-$ per formula unit (f.u.)

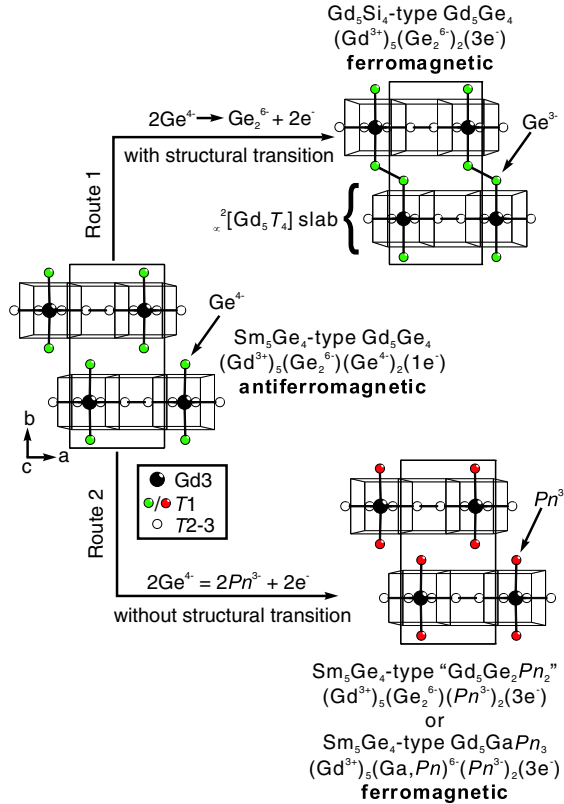


FIG. 1 (color online). Schematic diagram of the magnetostructural transition between Sm₅Ge₄- and Gd₅Si₄-type structures (route 1), and of the magnetic transition in the Sm₅Ge₄-type phase (route 2). Pn: pnictide elements.

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 ($3 e^-/\text{f.u.}$). Route 2 leads to a hypothetical “ $(\text{Gd}^{3+})_5(\text{Ge}_2^{6-})(\text{Pn}^{3-})_2(3e^-)$ ” 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 Sm₅Ge₄-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 ${}^2[\text{Gd}_5\text{T}_4]$ 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 4*f* 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 4*f* 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 4*p* states strongly hybridize with the Gd 5*d* 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 4*f* 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 $e^-/\text{f.u.}$, 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 5*d* 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 $e^-/\text{f.u.}$ In Fig. 2, one can clearly see that the E_F located just above the band gap in the spin-down channel and Gd 5*d* spin-up and spin-down states display a large exchange splitting, increasing the spin polarization of the conduction electrons. On average, the Gd 5*d* 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 Sm₅Ge₄-type phases without a structural transition, a Gd₅Ge₂Sb₂ sample with

TABLE I. Relative total energies and atom projected magnetic moments (in μ_B/atom) calculated for the Sm₅Ge₄-type compounds, Gd₅Ge₄, Gd₅Ge₂Sb₂, and Gd₅GaSb₃, by VASP with $U = 6.7$ eV and $J = 0.7$ eV.

	Gd ₅ Ge ₄		Gd ₅ Ge ₂ Sb ₂		Gd ₅ GaSb ₃	
	FM	AFM	FM	AFM	FM	AFM
E (eV)	0.200	0	0	0.592	0	0.422
$\mu(\text{Gd1})$	7.15	± 7.20	7.34	± 7.25	7.31	± 7.23
$\mu(\text{Gd2})$	7.16	± 7.20	7.31	± 7.24	7.29	± 7.24
$\mu(\text{Gd3})$	7.28	± 7.35	7.48	± 7.45	7.45	± 7.42

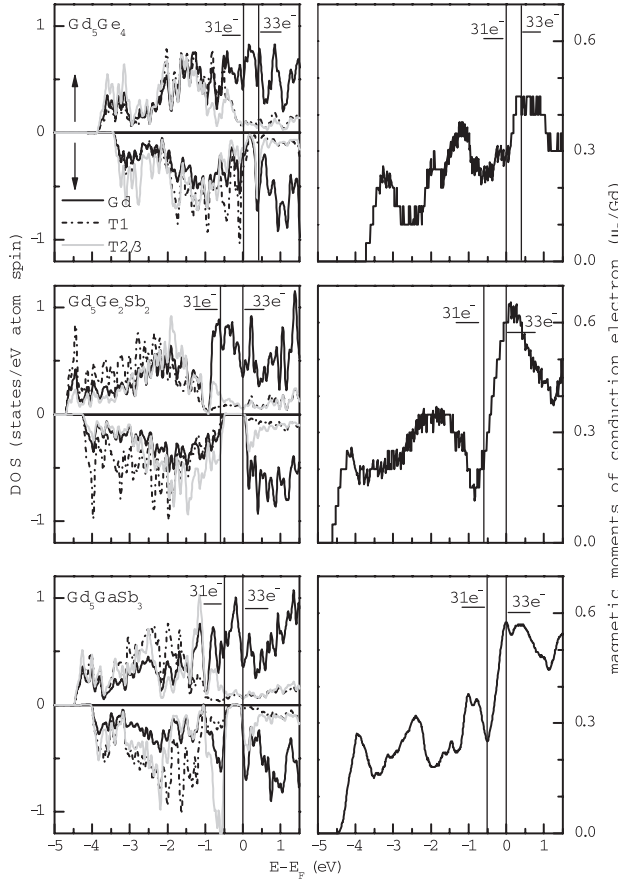


FIG. 2. Left panel: spin-polarized density of states (DOS) of the average $T1$, $T2/T3$, and Gd sites of Gd_5Ge_4 (top), $Gd_5Ge_2Sb_2$ (middle), and Gd_5GaSb_3 (low) in the ferromagnetic state. Right panel: magnetic moments of the conduction electrons for these phases. The dashed lines mark the valence electron count per formula within a rigid band approximation. The states of 31 and 33 e^- /formula correspond to Gd_5Ge_4 and $Gd_5Ge_2Sb_2/Gd_5GaSb_3$, respectively.

VEC = 33 e^- /f.u. was synthesized. The experimental details are described in Supplemental Material (SM) [27]. $Gd_5Ge_2Sb_2$, however, adopts the Eu_5Au_4 structure ($Cmca$) [Tables S1 and S2 in SM], rather than the desired Sm_5Ge_4 structure, in agreement with the previous reports [18,19]. In order to obtain the desired structure and VEC, the designed composition was adjusted to Gd_5GaSb_3 and Gd_5GaBi_3 . The single-crystal and powder x-ray diffraction studies show that both compounds adopt the Sm_5Ge_4 structure with broken interslab $T1$ - $T1$ 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

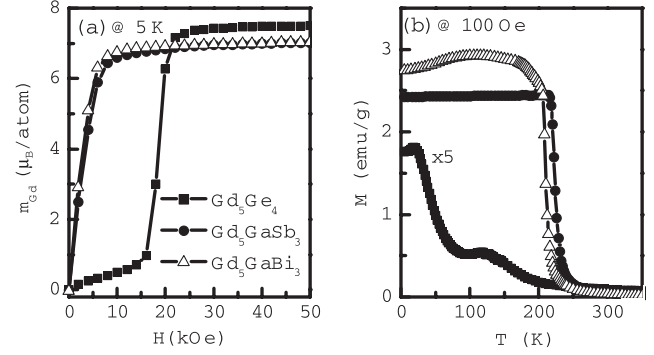


FIG. 3. (a) Magnetic field (H) dependence of the average Gd magnetic moment (μ_{Gd}) in Gd_5Ge_4 , Gd_5GaSb_3 , and Gd_5GaBi_3 at 5 K. (b) Magnetization (M) of these samples as a function of temperature (T) in a magnetic field of 100 Oe. The magnetization of Gd_5Ge_4 is enlarged by a factor of 5.

ground state of Gd_5Ge_4 is AFM and an AFM-FM transition couples with a $Sm_5Ge_4 - Gd_5Si_4$ structural transformation occurring around 18 kOe at 5 K, in agreement with the previous studies [9]. In contrast, Gd_5GaSb_3 and Gd_5GaBi_3 display a typical FM behavior and saturated magnetic moments of 7.01 and 7.03 μ_B/Gd , respectively, which are close to the theoretical moment of 7 μ_B ($4f^7$). Moreover, the temperature-dependent magnetization curves in Fig. 3(b) show that Gd_5Ge_4 remains in the AFM state in a low magnetic field, whereas Gd_5GaPn_3 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 Gd_5GaPn_3 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 Gd_5Ge_4 into the FM one in Gd_5GaPn_3 .

The collective magnetic behaviors of rare-earth-main-group materials, including $Gd_5Si_xGe_{4-x}$, 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 Gd_5Ge_4 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 $Gd_5Ge_2Sb_2$ use the crystallographic data identical to Gd_5Ge_4 , i.e., the same Gd-Gd distances, but shift the ground state from AFM to FM. The first-principles calculations for Gd_5GaSb_3 using experimental crystallographic data yield band characteristics similar to those of $Gd_5Ge_2Sb_2$ [Fig. 2]—e.g.,

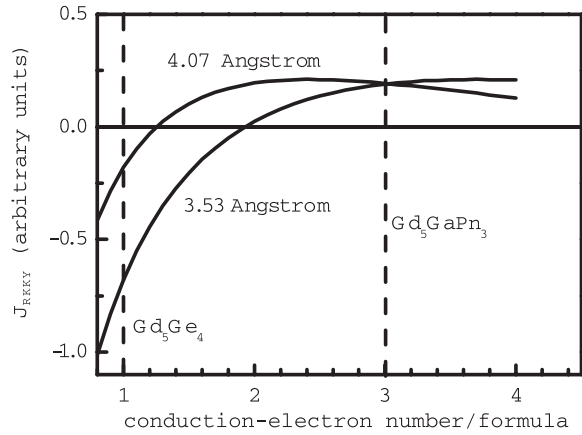


FIG. 4. Exchange interaction, J_{RKKY} , as a function of the conduction-electron number per formula in the Sm_5Ge_4 -type Gd_5Ge_4 compound. J_{RKKY} is estimated based on the RKKY model using a nearly free electron approximation. J_{RKKY} of short (3.53 Å) and long (4.07 Å) interslab Gd-Gd bonds is presented in the figure. Values for J_{RKKY} are normalized to equal -1 for 3.53 Å and $0.8 e^-/\text{formula}$.

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_5Ge_4 -type phases, the interslab Gd-Gd distance can support AFM interactions up to 5 Å [8]. However, the bonds in Gd_5GaPn_3 extend only up to 4.4 Å [Table S3 in SM], still within the AFM range. Third, recent experiments on $\text{Gd}_5\text{Ge}_{4-x}\text{P}_x$ and $\text{Gd}_5\text{Ge}_{4-x}\text{Sb}_x$ show that both systems are of the FM Sm_5Ge_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_{RKKY} , is given by $J_{\text{RKKY}} \propto F(2k_F R)$ with $F(x) = (x \cos x - \sin x)/x^4$ 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_5Ge_4 -type Gd_5Ge_4 compound, N_e is $1 e^-/\text{f.u.}$ ($= 4 e^-/\text{cell}$) in the conduction band and its J_{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_{RKKY} and hence magnetic coupling change sign with an increasing electron concentration. At $N_e = 3 e^-/\text{f.u.}$, corresponding to the $(\text{Gd}^{3+})_5(\text{Ga, Pn})^{6-}(\text{Pn}^{3-})_2(3e^-)$ formula isoelectronic with Gd_5Si_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_5Ge_4 changes to 0.422 eV/cell for Gd_5GaSb_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_5Ge_4 -type phases. Interslab AFM coupling of Gd_5Ge_4 can be transformed into the FM type by substitution of electron-rich 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 magnetoresponse 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

- [1] A. Planes *et al.*, *Magnetism and Structure in Functional Materials* (Springer, Berlin, 2005).
- [2] V. K. Pecharsky and K. A. Gschneidner, *Phys. Rev. Lett.* **78**, 4494 (1997).
- [3] O. Tegus, E. Brück, K. H. J. Buschow, and F. R. de Boer, *Nature (London)* **415**, 150 (2002).
- [4] B. G. Shen, J. R. Sun, F. X. Hu, H. W. Zhang, and Z. H. Cheng, *Adv. Mater.* **21**, 4545 (2009).
- [5] R. Kainuma *et al.*, *Nature (London)* **439**, 957 (2006).
- [6] G. J. Miller, *Chem. Soc. Rev.* **35**, 799 (2006).
- [7] V. K. Pecharsky and K. A. Gschneidner, *Pure Appl. Chem.* **79**, 1383 (2007).
- [8] W. Choe, V. K. Pecharsky, A. O. Pecharsky, K. A. Gschneidner, V. G. Young, and G. J. Miller, *Phys. Rev. Lett.* **84**, 4617 (2000).
- [9] V. K. Pecharsky, A. P. Holm, K. A. Gschneidner, and R. Rink, *Phys. Rev. Lett.* **91**, 197204 (2003).
- [10] D. Paudyal, Y. Mudryk, V. K. Pecharsky, and K. A. Gschneidner, *Phys. Rev. B* **82**, 144413 (2010).
- [11] Y. Mozharivskiy, W. Choe, A. O. Pecharsky, and G. J. Miller, *J. Am. Chem. Soc.* **125**, 15183 (2003).
- [12] V. Svitlyk, G. J. Miller, and Y. Mozharivskiy, *J. Am. Chem. Soc.* **131**, 2367 (2009).
- [13] L. M. Wu, S.-H. Kim, and D.-K. Seo, *J. Am. Chem. Soc.* **127**, 15682 (2005).
- [14] P. H. Tobash, S. Bobev, J. D. Thompson, and J. L. Sarrao, *Inorg. Chem.* **48**, 6641 (2009).
- [15] Q. X. Xie, C. Kubata, M. Wörle, and R. Nesper, *Z. Anorg. Allg. Chem.* **634**, 2469 (2008).
- [16] J. Yao, P. Wang, and Y. Mozharivskiy, *Chem. Mater.* **24**, 552 (2012).
- [17] C. Magen, Z. Arnold, L. Morellon, Y. Skorokhod, P. A. Algarabel, M. R. Ibarra, and J. Kamarad, *Phys. Rev. Lett.* **91**, 207202 (2003).

- [18] A. S. Chernyshov, Ya. S. Mudryk, V. K. Pecharsky, and K. A. Gschneidner, *J. Appl. Phys.* **99**, 08Q102 (2006).
- [19] A. S. Chernyshov, Ya. Mudryk, D. Paudyal, V. K. Pecharsky, K. A. Gschneidner, D. L. Schlagel, and T. A. Lograsso, *Phys. Rev. B* **80**, 184416 (2009).
- [20] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [21] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- [22] G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- [23] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [24] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [25] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, *Phys. Rev. B* **57**, 1505 (1998).
- [26] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, *J. Phys. Condens. Matter* **9**, 767 (1997).
- [27] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.110.077204> for synthesis, structural analyses, and magnetization data.
- [28] Y. Mudryk, D. Paudyal, V. K. Pecharsky, and K. A. Gschneidner, *Phys. Rev. B* **77**, 024408 (2008).
- [29] Y. Y. J. Cheung, V. Svitlyk, and Y. Mozharivskyj, *J. Magn. Magn. Mater.* **331**, 237 (2013).
- [30] J. Callaway, *Quantum Theory of the Solid State* (Academic, New York, 1991), p. 855.