2010

Influence of Y substitutions on the magnetism of Gd5Ge4

Durga Paudyal
Iowa State University, dpaudyal@iastate.edu

Yaroslav Mudryk
Iowa State University, slavkomk@ameslab.gov

Vitalij K. Pecharsky
Iowa State University, vitkp@ameslab.gov

Sumohan Misra
Iowa State University, misra@iastate.edu

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

See next page for additional authors

Influence of Y substitutions on the magnetism of Gd5Ge4

Abstract
The interrelation between the specific crystallographic positions and their influence on the magnetism of neighboring atoms is examined from first principles electronic structure calculations using the Gd5Ge4 compound as a model system. The predicted preferences of the specific occupations by nonmagnetic yttrium atoms and the resulting magnetism of substituted Gd5Ge4 have been confirmed, respectively, by single crystal x-ray diffraction and magnetization experiments.

Disciplines
Materials Chemistry | Metallurgy | Other Chemistry | Physical Chemistry

Comments
The following article appeared in Journal of Applied Physics 107, 09A908 (2010); 1 and may be found at doi:10.1063/1.3349231.

Authors
Durga Paudyal, Yaroslav Mudryk, Vitalij K. Pecharsky, Sumohan Misra, Gordon J. Miller, and Karl A. Gschneidner Jr.

AIP Journal of Applied Physics

Influence of Y substitutions on the magnetism of Gd 5 Ge 4

Durga Paudyal, Y. Mudryk, V. K. Pecharsky, S. Misra, G. J. Miller, and K. A. Gschneidner Jr.

Citation: Journal of Applied Physics **107**, 09A908 (2010); doi: 10.1063/1.3349231
View online: http://dx.doi.org/10.1063/1.3349231
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/107/9?ver=pdfcov
Published by the AIP Publishing

Influence of Y substitutions on the magnetism of Gd_5Ge_4

Durga Paudyal,[1,a)] Y. Mudryk,[1] V. K. Pecharsky,[1,2] S. Misra,[1,3] G. J. Miller,[1,3] and K. A. Gschneidner, Jr.[1,2]
[1]*The Ames Laboratory, U.S. Department of Energy, Iowa State University, Ames, Iowa 50011-3020, USA*
[2]*Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-2300, USA*
[3]*Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111, USA*

(Presented 22 January 2010; received 28 October 2009; accepted 2 December 2009; published online 19 April 2010)

The interrelation between the specific crystallographic positions and their influence on the magnetism of neighboring atoms is examined from first principles electronic structure calculations using the Gd_5Ge_4 compound as a model system. The predicted preferences of the specific occupations by nonmagnetic yttrium atoms and the resulting magnetism of substituted Gd_5Ge_4 have been confirmed, respectively, by single crystal x-ray diffraction and magnetization experiments.
 [doi:10.1063/1.3349231]

I. INTRODUCTION

After the discovery of the giant magnetocaloric system $Gd_5Si_2Ge_2$,[1] one of the end members of the $Gd_5Si_{4-x}Ge_x$ series, namely, Gd_5Ge_4, became a model material to understand a combination of strong magnetostriction,[2] magnetoresistance,[3] and magnetocaloric[4] phenomena that occur in the same system. Gd_5Ge_4 crystallizes in the orthorhombic Sm_5Ge_4-type [O(II)] structure containing six inequivalent sites in the unit cell: Gd1 (4*c*), Gd2 (8*d*) and Gd3 (8*d*), Ge1 (4*c*), Ge2 (4*c*), and Ge3 (8*d*).[5] The magnetic ground state of the O(II) structure is antiferromagnetic (AFM).[6] However, AFM O(II) Gd_5Ge_4 easily transforms to the ferromagnetic (FM) orthorhombic Gd_5Si_4-type [O(I)] structure upon application of a 1.6 T magnetic field.[7] In both structures, 5 monolayers of Ge, Gd, Gd+Ge, Gd, and Ge form pseudotwo-dimensional nanoslabs. The slabs are quasi-infinite in the *ac*-plane, but they are only ~7 Å thick along the *b* axis.[5]

During the AFM [O(II)] to FM [O(I)] transformation, the neighboring slabs of Gd_5Ge_4 that are themselves FM, shift so that the Ge3–Ge3 distances contract and the Ge3 4*p* spin up states and the Gd1 5*d* spin up states hybridize favoring FM exchange interactions between the Gd atoms that belong to different slabs.[8] In the reverse transformation, the same distances elongate and the Ge3 4*p* spin down states and the Gd1 5*d* spin down states hybridize favoring AFM interslab exchange interactions.[8] The calculated magnetic moments of inequivalent Gd atoms clearly indicate that the Gd1 atoms, which form both the inter- and intraslab –Gd1–Ge–Ge–Gd1– networks, have higher 5*d* moments compared to the other inequivalent Gd2 and Gd3 atoms.[9,10]

Recent total energy calculations performed as a function of shear distortion confirmed the first-order nature of the phase transformation between FM Gd_5Si_4-type orthorhombic O(I) and the AFM Sm_5Ge_4-type orthorhombic O(II) structure in Gd_5Ge_4 in agreement with experiment.[9] The electronic structure calculations also showed that the AFM O(II) Gd_5Ge_4 phase is the ground state. The conduction electron band splitting caused by the indirect 4*f*-4*f* exchange is lower in the O(II) Gd_5Ge_4 compared to the O(I) Gd_5Ge_4. This is associated with the longer interslab Ge–Ge distances and larger hybridization in the antibonding states of Gd and Ge atoms in AFM O(II) Gd_5Ge_4.[8]

The origin of antiferromagnetism and ferromagnetism of Gd_5Ge_4 has also been studied through evaluating the indirect 4*f*-4*f* exchange interactions and analysis of 4*f*-5*d* exchange energies and the total energies of different spin configurations. These calculations show short range FM but long range AFM coupling between Gd atoms in the O(II) Gd_5Ge_4 and only FM coupling is found in the O(I) structure of Gd_5Ge_4.[8]

The investigation of the magnetism of Gd_5T_4, where T = Si, Ge brings an important question: what happens with the electronic structure if we replace some of the Ge sites with Si? The total energy versus unit-cell volume calculation confirmed a first-order phase transformation between the O(II) $Gd_5Si_{0.5}Ge_{3.5}$ and O(I) $Gd_5Si_{0.5}Ge_{3.5}$, in agreement with the experiment.[11] The calculations also predicted that substituted Si plays a role similar to the effect of magnetic field by creating chemical pressure, and transforms the ground state from the AFM O(II) structure to FM O(I) structure without the application of magnetic field.

After understanding the importance of the T sites in Gd_5T_4, an interesting question remains: what will happen with the magnetism of Gd_5Ge_4 if one substitutes different Gd sites by nonmagnetic rare earths such as Y with a similar atomic size? Our aim here is to understand how these substituted atoms affect the electronic structure allowing for a better control of the magnetic structure and properties of Gd_5Ge_4.

II. THEORY

The scalar relativistic tight binding linear muffin tin orbital[12] calculations have been performed within the local spin density approximation including Hubbard *U* parameter

a)Electronic mail: durga@ameslab.gov.

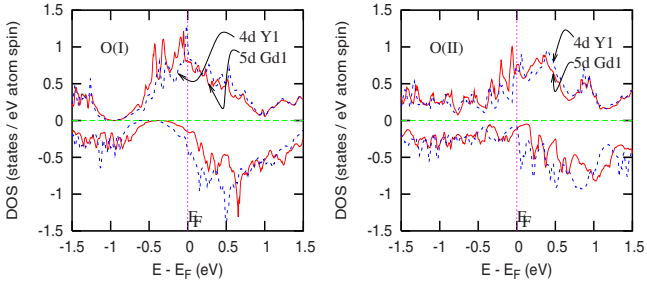

FIG. 1. (Color online) The 5*d* DOS of the Gd1 atom (solid line) in the O(I) and O(II) structures of Gd_5Ge_4 are compared with the 4*d* DOS of the Y1 atom (dashed line) when it replaces the Gd atoms occupying the Gd1 sites.

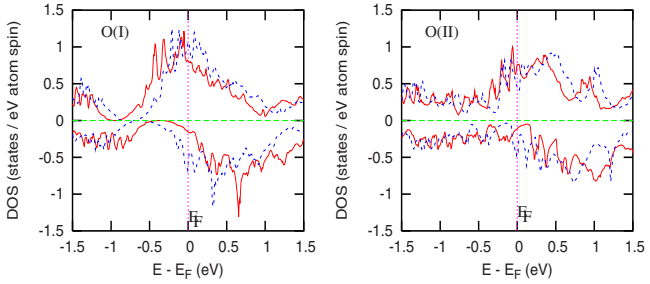

FIG. 2. (Color online) The 5*d* DOS of the Gd1 atom in the O(I) and O(II) structures of Gd_5Ge_4 (solid lines) are compared with the 5*d* DOS of the Gd1 atom when the Gd2 and Gd3 sites are replaced by Y atoms (dashed lines).

(LSDA+U) approach.[13,14] We used $U=6.7$ eV and $J=0.7$ eV—the well known values for Gd atoms. The conventional von Barth and Hedin parameterization of the LSDA (Ref. 15) has been adopted. A total of 125 special k points have been used in the irreducible part of the Brillouin zone for k space integration.

The FM calculations for the O(I) and O(II) structures of Gd_5Ge_4 show higher value of 5*d* magnetic moment on Gd1 compared to the 5*d* moments of other inequivalent Gd atoms, which suggests that Gd1 site plays a major role in the magnetism of Gd_5Ge_4. To test this hypothesis we have theoretically selectively replaced Gd atoms by nonmagnetic Y atoms. First we have calculated the formation energies from the corresponding total energies which show that Y atoms prefer the Gd1 site.

When Gd1 atoms are replaced by Y atoms in the O(I) and O(II) structures of Gd_5Ge_4, the *d* density of states (DOS) at the Fermi level with and without replacement does not show much difference (Fig. 1) but the integrated DOS up to the Fermi level and the splitting of the *d* bands (the difference between the spin up and spin down band centers) at the Fermi level decrease significantly reducing the *d* moments of this site by 48% and 68%, respectively. This indicates that changes induced by Y substitution in the integrated DOS (decrease in spin up integrated DOS up to the Fermi level and increase in the spin down integrated DOS up to the Fermi level) and the band splitting at the Fermi level play an important role in the reduction in *d* moments. The substantial decrease in the *d* moments of this site is an indicative that it is an important site in determining the magnetism of substituted Gd_5Ge_4. The yttrium substitution in Gd1 site also slightly lowers the 5*d* moments of Gd2 and Gd3 indicating that the neighboring sites are also affected by the replacement of Gd1 site in the network of a slab.

When Gd2 and Gd3 are replaced by Y atoms, the spin up 5*d* DOS of Gd1 slightly shifts to higher energy and the spin down DOS shifts to lower energy side (Fig. 2) resulting in a small decrease in the spin up integrated DOS and increase in the spin down DOS. There is also small [12% in the O(I) and 2% in the O(II)] decrease in the 5*d* band splitting of Gd1 atom. As a result there is only 33% and 16% reduction in the 5*d* moments of Gd1, in the O(I) and O(II) structures, respectively. This shows that placing Y in Gd2 and Gd3 positions has a weak effect in reducing the 5*d* moments of Gd1 site. The calculations also show that the 4*d* moments of Y2 and Y3 are small (less than 0.1 μ_B) in both the O(I) and O(II) structures. This indicates that the 5*d* Gd and 4*d* Y hybridization is weak when the Gd2 and Gd3 sites are replaced by Y atoms suggesting that the Gd1–Gd1 exchange interactions are stronger compared to those for other Gd–Gd pairs, and thus the Gd1 site has stronger impact on the compound's magnetism.

The purely nonmagnetic DOS in Gd_5Ge_4 were calculated by replacing all Gd atoms by nonmagnetic Y atoms (Fig. 3), i.e., for "Y_5Ge_4." At the Fermi level the 4*d* partial DOS of Y1 is higher compared to that of the 4*d* partial DOS of Y2 and Y3. The higher 4*d* partial DOS of Y1 is a clear indication that in both structures this site should have the largest magnetic moment upon replacement by a magnetic, e.g., Gd, atom. It is quite interesting to point out that the band centers of Y2 and Y3 atoms are nearly identical and both are different from the band center of Y1 site for O(I) Y_5Ge_4. In the case of O(II) Y_5Ge_4 all three inequivalent Y sites differ substantially. This indicates that while replacing inequivalent Y sites by magnetic atoms, the magnetic behavior in the O(II) structure will be different than that of the O(I) structure.

III. EXPERIMENT

The single crystal x-ray diffraction data confirm that the Y atom prefers to occupy the Gd1 site[16] as predicted from the calculated formation energy. As a result, the magnetic measurements (Fig. 4) show that small substitutions of Y, on the Gd1 site result in drastic changes in magnetism of Gd_5Ge_4. As shown in Fig. 4, the magnetization as a function of magnetic field clearly indicates AFM behavior at 15 K in applied fields as high as 50 kOe. The magnetization as a function of temperature in a 20 kOe magnetic field shows only an AFM to paramagnetic transition at $T_N \sim 117$ K (Fig.

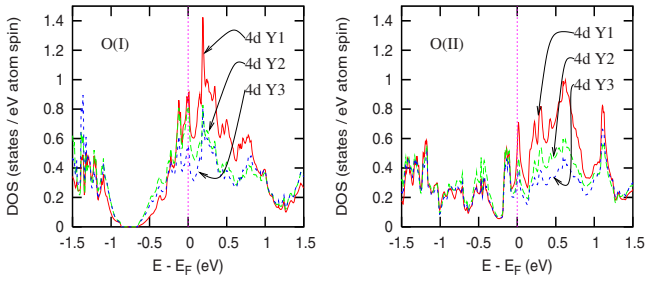

FIG. 3. (Color online) The 4*d* partial DOS of inequivalent Y atoms in the O(I) and O(II) "Y_5Ge_4" structures.

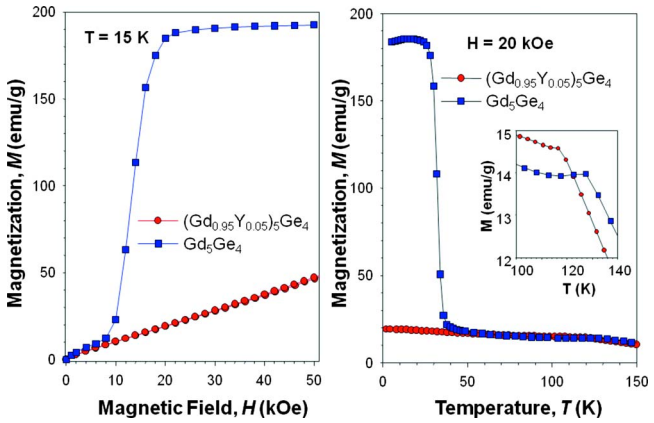

FIG. 4. (Color online) Magnetization vs field at 15 K (left panel) and magnetization vs temperature in a 20 kOe magnetic field (right panel) in Gd_5Ge_4 and $(Gd_{0.95}Y_{0.05})_5Ge_4$. The inset in the right panel shows T_N=117 K in $(Gd_{0.95}Y_{0.05})_5Ge_4$.

4) in $(Gd_{0.95}Y_{0.05})_5Ge_4$. There is no field induced FM behavior in $(Gd_{0.95}Y_{0.05})_5Ge_4$ which confirms that the neighboring slabs are no longer ferromagnetically stacked when the Gd1 site is replaced by Y.

IV. CONCLUSION

The three Gd sites in the O(I) and O(II) Gd_5Ge_4 structures show different 5*d* exchange splitting, integrated densities of states and magnetic moments. The substantial lowering of the *d* moments while replacing Gd1 site by a non magnetic Y atom, is in contrast to minute change when Y is substituted on the Gd2 and Gd3 sites. These calculations show that this site plays a crucial role in the determination of the magnetism in Gd_5Ge_4. The Gd1–Gd1 exchange interactions are stronger compared to those for other Gd–Gd pairs. The experiments confirm that Y atoms prefer to occupy Gd1 sites and have strong effect in the magnetism of the parent Gd_5Ge_4.

ACKNOWLEDGMENTS

The Ames Laboratory is operated by Iowa State University of Science and Technology for the U.S. Department of Energy under Contract No. DE-AC02-07CH11358. Work at Ames Laboratory is supported by the Office of Basic Energy Sciences, Materials Sciences Division of the Office of Science.

[1]V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[2]C. Magen, L. Morellon, P. A. Algarabel, C. Marquina, and M. R. Ibarra, J. Phys.: Condens. Matter **15**, 2389 (2003).
[3]E. M. Levin, V. K. Pecharsky, K. A. Gschneidner, Jr., and G. J. Miller, Phys. Rev. B **64**, 235103 (2001).
[4]V. K. Pecharsky, A. P. Holm, K. A. Gschneidner, Jr., and R. Rink, Phys. Rev. Lett. **91**, 197204 (2003).
[5]V. K. Pecharsky and K. A. Gschneidner, Jr., Pure Appl. Chem. **79**, 1383 (2007).
[6]L. Tan, A. Kreyssig, J. W. Kim, A. I. Goldman, R. J. McQueeney, D. Wermeille, B. Sieve, T. A. Lograsso, D. L. Schlagel, S. L. Budko, V. K. Pecharsky, and K. A. Gschneidner, Jr., Phys. Rev. B **71**, 214408 (2005).
[7]Y. Mudryk, A. P. Holm, K. A. Gschneidner, Jr., and V. K. Pecharsky, Phys. Rev. B **72**, 064442 (2005).
[8]D. Paudyal, V. K. Pecharsky, and K. A. Gschneidner, Jr., J. Phys.: Condens. Matter **20**, 235235 (2008).
[9]D. Paudyal, V. K. Pecharsky, K. A. Gschneidner, Jr., and B. N. Harmon, Phys. Rev. B **75**, 094427 (2007).
[10]D. Paudyal, V. K. Pecharsky, K. A. Gschneidner, Jr., and B. N. Harmon, Phys. Rev. B **73**, 144406 (2006).
[11]Y. Mudryk, D. Paudyal, V. K. Pecharsky, and K. A. Gschneidner, Jr., Phys. Rev. B **77**, 024408 (2008).
[12]O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).
[13]V. I. Anisimov, F. Aryasetiawan, and A. I. Liechtenstein, J. Phys.: Condens. Matter **9**, 767 (1997).
[14]B. N. Harmon, V. P. Antropov, A. I. Liechtenstein, I. V. Solovyeb, and V. I. Anisimov, J. Phys. Chem. Solids **56**, 1521 (1995).
[15]U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
[16]S. Misra and G. J. Miller, J. Am. Chem. Soc. **130**, 13900 (2008).