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

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

Part of the Materials Chemistry Commons, Metallurgy Commons, Other Chemistry Commons, and the Physical Chemistry Commons

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/chem_pubs/697. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.
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.

Rights
Copyright 2010 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.

Authors
Influence of Y substitutions on the magnetism of Gd$_5$Ge$_4$


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

Articles you may be interested in
Magnetic properties and local microstructures in Zn-doped YMnO$_3$

Ferromagnetic structures in Mn$_2$CoGa and Mn$_2$CoAl doped by Co, Cu, V, and Ti

Absence of ferromagnetism in Mn-doped tetragonal zirconia
J. Appl. Phys. 110, 043929 (2011); 10.1063/1.3626788

Computational study of copper ferrite (CuFe$_2$O$_4$)

Structural and magnetic properties of Co/α-Al$_2$O$_3$/Fe magnetic tunneling junction system: Ab initio investigations
Influence of Y substitutions on the magnetism of Gd$_5$Ge$_4$


1The Ames Laboratory, U.S. Department of Energy, Iowa State University, Ames, Iowa 50011-3020, USA
2Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-2800, USA
3Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111, USA

(Received 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$_5$Ge$_4$ compound as a model system. The predicted preferences of the specific occupations by nonmagnetic yttrium atoms and the resulting magnetism of substituted Gd$_5$Ge$_4$ have been confirmed, respectively, by single crystal x-ray diffraction and magnetization experiments.


I. INTRODUCTION

After the discovery of the giant magnetocaloric system Gd$_5$Si$_2$Ge$_2$, one of the end members of the Gd$_5$Si$_{4-x}$Ge$_x$ series, namely, Gd$_5$Ge$_4$, became a model material to understand a combination of strong magnetostriiction, magnetoresistance, and magnetocaloric phenomena that occur in the same system. Gd$_5$Ge$_4$ crystallizes in the orthorhombic Sm$_5$Ge$_4$-type structure containing six inequivalent sites in the unit cell: Gd1 (4c), Gd2 (8d) and Gd3 (8d), Ge1 (4c), Ge2 (4c), and Ge3 (8d). The magnetic ground state of the O(II) structure is antiferromagnetic (AFM). However, AFM O(II) Gd$_5$Ge$_4$ easily transforms to the ferromagnetic (FM) orthorhombic Gd$_5$Si$_{4-x}$Ge$_{x}$-type O(I) structure upon application of a 1.6 T magnetic field. In both structures, 5 monolayers of Ge, Gd, Gd+Ge, Gd, and Ge form pseudo-two-dimensional nanoslabs. The slabs are quasi-infinite in the ac-plane, but they are only ~7 Å thick along the b axis.

During the AFM [O(II)] to FM [O(I)] transformation, the neighboring slabs of Gd$_5$Ge$_4$ that are themselves FM, shift so that the Ge3–Ge3 distances contract and the Ge3 4p spin up states and the Gd1 5d spin up states hybridize favoring FM exchange interactions between the Gd atoms that belong to different slabs. In the reverse transformation, the same distances elongate and the Ge3 4p spin down states and the Gd1 5d spin down states hybridize favoring AFM inter-slab exchange interactions. 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 5d moments compared to the other inequivalent Gd2 and Gd3 atoms.

Recent total energy calculations performed as a function of shear distortion confirmed the first-order nature of the phase transformation between FM Gd$_5$Si$_2$-type orthorhombic O(I) and the AFM Sm$_5$Ge$_4$-type orthorhombic O(II) structure in Gd$_5$Ge$_4$ in agreement with experiment. The electronic structure calculations also showed that the AFM O(II) Gd$_5$Ge$_4$ phase is the ground state. The conduction electron band splitting caused by the indirect 4f-4f exchange is lower in the O(II) Gd$_5$Ge$_4$ compared to the O(I) Gd$_5$Ge$_4$. 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$_5$Ge$_4$.

The origin of antiferromagnetism and ferromagnetism of Gd$_5$Ge$_4$ has also been studied through evaluating the indirect 4f-4f exchange interactions and analysis of 4f-5d 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$_5$Ge$_4$ and only FM coupling is found in the O(I) structure of Gd$_5$Ge$_4$.

The investigation of the magnetism of Gd$_5$T$_4$, 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$_5$Si$_{0.5}$Ge$_{3.5}$ and O(I) Gd$_5$Si$_{0.5}$Ge$_{3.5}$, in agreement with the experiment.

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$_5$T$_4$, an interesting question remains: what will happen with the magnetism of Gd$_5$Ge$_4$ 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$_5$Ge$_4$.

II. THEORY

The scalar relativistic tight binding linear muffin tin orbital calculations have been performed within the local spin density approximation including Hubbard U parameter.
(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 shows much difference at the Fermi level with and without replacement does not prefer the Gd1 site.

The calculations also show that the 4\(d\) moments of Y2 and Y3 are small (less than 0.1 \(\mu_B\)) 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 “Y5Ge4.” 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) Y3Ge4. In the case of O(II) Y3Ge4 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 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. 3).

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).

FIG. 3. (Color online) The 4\(d\) partial DOS of inequivalent Y atoms in the O(I) and O(II) “Y5Ge4” structures.
IV. CONCLUSION

The three Gd sites in the O(I) and O(II) Gd₅Ge₄ structures show different 5d 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 Gd₅Ge₄. 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 Gd₅Ge₄.

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.