Controlling Magnetism of a Complex Metallic System Using Atomic Individualism

Y. Mudryk and D. Paudyal
The Ames Laboratory, US Department of Energy, Iowa State University, Ames, Iowa 50011-3020, USA

V. K. Pecharsky and K. A. Gschneidner, Jr.
The Ames Laboratory, U.S. Department of Energy, Iowa State University, Ames, Iowa 50011-3020, USA
and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-2300, USA

S. Misra and G. J. Miller
The Ames Laboratory, U.S. Department of Energy, Iowa State University, Ames, Iowa 50011-3020, USA
and Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111, USA
(Received 2 March 2010; published 2 August 2010)

When the complexity of a metallic compound reaches a certain level, a specific location in the structure may be critically responsible for a given fundamental property of a material while other locations may not play as much of a role in determining such a property. The first-principles theory has pinpointed a critical location in the framework of a complex intermetallic compound—Gd_5Ge_4—that resulted in a controlled alteration of the magnetism of this compound using precise chemical tools.

DOI: 10.1103/PhysRevLett.105.066401 PACS numbers: 71.20.Eh, 81.30.Hd

The contribution that each chemical element brings to the behavior of the whole molecule or the crystal can be vastly different. The atoms of the same element may also behave differently depending on their location in a molecule and this is well known in the organic world, e.g., in DNA [1]. Here, the contribution from different groups of atoms (genes) varies as needed. The inorganic condensed matter world is quite different. The crystalline objects, being in effect large macromolecules, exhibit nearly perfect order. Each atom, depending on its nature and location, contributes to a total electronic structure, which determines the ground state properties of the whole system [2]. Here, individuality is rare, but useful cooperative phenomena such as magnetic ordering and superconductivity are common (even though organic compounds may also exhibit cooperative effects [3]). In this Letter we show that at certain levels of complexity, a typical metallic material may allow for clear individualism of the constituting atoms by demonstrating that a single site occupied by the Gd atoms is much more active than all of the other Gd sites when it comes to bringing the ferromagnetic (FM) order in a complex crystal structure of gadolinium germanide.

Deciphering how a lattice is responsible for a given combination of magnetic properties is interesting and important, yet it is a difficult task. For example, neutron diffraction may identify atoms that carry larger magnetic moments than the others, but the technique is nearly helpless for Gd and Gd-rich compounds because the naturally occurring mixture of Gd isotopes has an extremely large neutron absorption cross section. Even after isolating the needed isotopes of Gd to make a neutron scattering experiment possible, knowing the magnetic moments of the individual atoms may not be enough to understand which Gd site, if any, is critically responsible for the magnetism of a complex lattice such as Gd_5Ge_4, in which indirect magnetic exchange interactions are prevalent [4].

The Gd_5Ge_4 compound has been broadly studied due to an impressive combination of interesting and potentially important properties, such as anisotropic magnetostriction, magnetoresistivity, and unusual kinetics of the magnetostructural transition [5–7]. FM order in this compound cannot be induced by cooling alone, but a magnetic field as low as 10 kOe triggers ferromagnetism via a first-order phase transition that also involves a major rearrangement of the crystal structure of the material [8]. Similar effects occur when either hydrostatic or chemical pressure is applied to this system [9]. The extraordinary responsiveness to relatively weak external stimuli makes Gd_5Ge_4 and related compounds a phenomenal playground for condensed matter science.

The crystal structure of Gd_5Ge_4 is best represented as a stacking of two-dimensional slabs containing three crystallographically different Gd positions. Gd_1 located inside the slabs is connected to other Gd_1 atoms from the neighboring slabs via interslab Ge-Ge bonds [10,11]. Gd_2 and Gd_3 can interact directly with one another (Fig. 1) [8]. The presence or absence of strong Ge-Ge bonds between the slabs determines whether the compound has the FM O(I) or the antiferromagnetic (AFM) O(II) structure [11], respectively (see Refs. [12,13] for a detailed description of these two structures that belong to the same space group symmetry $Pnma$, and the origin of the structural notation).

Chemical substitutions play a major role in this system. When Ge is partially replaced with Si, the magnetostructural transition occurs on cooling without the application of a magnetic field. This happens because chemical pressure enhances ferromagnetism [14]. However, since Ge and Si atoms carry no magnetic moment, the full understanding of

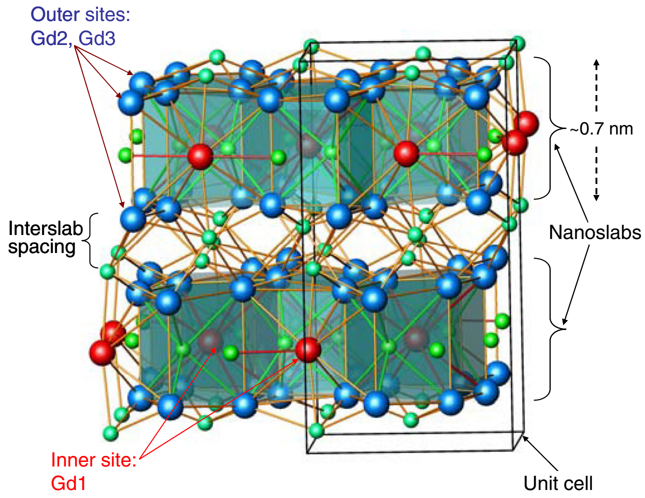

FIG. 1 (color online). Crystal structure of the nonferromagnetic Gd_5Ge_4 phase. The germanium atoms are shown as small green (light gray) spheres.

the magnetism of $Gd_5(Ge_{1-x}Si_x)_4$ compounds requires consideration of the Gd behavior. The complexity of the Gd_5Ge_4 structure, and therefore, the potential sensitivity of its framework to the nature of the substituting atoms [15,16] may lead to an unprecedented precision in replacements of crystallographically different, magnetically active Gd atoms by smaller (Sc or Lu), larger (La) or nearly identical in size (Y) nonmagnetic rare earth elements. If the fraction of replaced atoms remains small, trivial dilution effects may be avoided or minimized, and thus the role that different Gd atom sites play in defining the magnetic properties of this complex system may be clarified. With this in mind, we first proceed with modeling substitutions of gadolinium using lanthanum and lutetium, and then attempt to validate these modeling results in designed experiments.

The first-principles calculations have been performed using the scalar relativistic version of the tight binding linear muffin-tin orbital (TB-LMTO) [17] method including mass velocity and Darwin correction within the framework of the local spin density approximation [18] with the on site Coulomb parameter (LSDA + U) approach [19]. In order to accurately position the occupied and unoccupied $4f$ states of Gd, $U = 6.7$ eV and $J = 0.7$ eV [20] have been used. A total of 125 special k points in the irreducible part of the Brillouin zone were used for k space integrations in both O(I) and O(II) polymorphs. When spin orbit coupling is included in calculations, the resulting changes in the total energy (less than 10 μeV/Gd) and magnetic moments ($\sim 0.02\mu_B$/Gd) are negligible, and therefore, the results are shown without considering spin orbit coupling.

The 5 g samples were prepared by arc-melting of the pure elements (the rare earth metals were 99.95+ wt. % pure with respect to all other elements in the periodic table [21]) in an argon atmosphere and heat treated at 1000 °C for 48 hours in helium-filled quartz tubes. Room temperature crystal structures were determined using x-ray single crystal diffraction (Bruker Smart Apex CCD diffractometer). Low-temperature, x-ray powder diffraction experiments were performed in zero and applied magnetic fields using the x-ray powder diffractometer described elsewhere [22]. The dc magnetization was measured in a Quantum Design MPMS-XL7 magnetometer.

First, it is important to know whether preferential substitutions are thermodynamically feasible. To do so, formation energies were calculated as $E_f = E_{Gd_{5-x}M_xGe_4} - (5-x)E_{Gd} - 4E_{Ge} - xE_M$, where E and x represent total energies and concentrations, respectively, while placing M (La or Lu) atoms in individual positions of the Gd atoms in both the O(I) and O(II) Gd_5Ge_4. As shown in Table I, the lowest (most negative) formation energies are found when La replaces Gd_2 and when Lu replaces Gd_1 in both O(I) and O(II) Gd_5Ge_4. The same result is obtained for ΔE of the process $Gd_5Ge_4 + xM \rightarrow Gd_{5-x}M_xGe_4 + x$Gd. This theoretical prediction is in general agreement with the previous experimental results obtained for the system with Yb, which exhibits mixed valence [23]. But what, if any, would be the effect of such substitutions on magnetism?

Prior theoretical investigations of Gd_5Ge_4 [24,25] indicate that the magnetic moments of the conduction electrons (mainly $5d$) of the three inequivalent Gd atoms are substantially different. For example, in the FM-O(I) structure, the $5d$ moments of Gd_1 ($0.62\mu_B$) exceed those of Gd_2 ($0.50\mu_B$) and Gd_3 ($0.39\mu_B$). We note that each Gd atom in both polymorphs has a $4f$ moment totaling $7\mu_B$, which polarize the conduction electrons through indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions. These interactions cause exchange splitting in the majority and minority spin bands of conduction electrons, giving rise to $5d$ magnetic moments. We find that both the exchange splitting and magnetic moments of $5d$ electrons decrease substantially when Gd_1 is replaced either by Lu or

TABLE I. Exchange interactions, J_0, estimated from the total energy difference between AFM and FM configurations of Gd atoms in O(I) and O(II) structures. The values in the square brackets are the formation energies, E_f, with Lu and La substitutions in the corresponding independent sites of Gd. The lowest values of E_f are highlighted in bold.

Composition (substitution)	J_0 (meV/Gd) [E_f (eV/cell)] O(I)-type	O(II)-type
Gd_5Ge_4	41.1	−16.8
Gd_4LuGe_4 (Lu in Gd_1)	19.0 [−**27.458**]	−5.0 [−**27.501**]
$Gd_3Lu_2Ge_4$ (Lu in Gd_2)	39.5 [−24.588]	−16.4 [−24.613]
$Gd_3Lu_2Ge_4$ (Lu in Gd_3)	39.4 [−27.349]	−16.3 [−26.951]
$GdLu_4Ge_4$ (Lu in $Gd_{2,3}$)	36.9 [−24.578]	−14.1 [−25.148]
Gd_4LaGe_4 (La in Gd_1)	23.8 [−25.932]	−15.4 [−26.315]
$Gd_3La_2Ge_4$ (La in Gd_2)	40.0 [−**28.915**]	−16.5 [−**28.537**]
$Gd_3La_2Ge_4$ (La in Gd_3)	39.2 [−24.243]	−16.4 [−23.505]
$GdLa_4Ge_4$ (La in $Gd_{2,3}$)	31.9 [−25.890]	−16.0 [−25.601]

La in both polymorphs of Gd_5Ge_4, but the changes are much smaller when Gd_2 and Gd_3 sites are occupied by Lu or La (Fig. 2). Note, that the La and the Lu substitutions here and below are modeled with the ‘‘ideal substitution’’ approximation, where neither the potential volume changes nor the changes in atomic environment are taken into account, and do not represent the actual structures because the study is focused on the role of Gd positions in Gd_5Ge_4 compound. These results indicate that the Gd_1 site plays a major role in determining the magnetic behavior of Gd_5Ge_4.

The differences in the moments of conduction electrons of the independent Gd atoms are observed because spin polarization depends on the nearest neighbor environment [4,27]. Experimental studies [28,29] show that the neighboring slabs, which are themselves FM, are coupled ferromagnetically in O(I)-Gd_5Ge_4, but the slabs are AFM aligned in the O(II) polymorph. Thus, magnetism of this material can be represented using the Heisenberg model by considering interactions between the nearest neighbor slabs. One of the ways to estimate these interactions is by calculating the total energy difference between the AFM and FM aligned nearest neighbor slabs, i.e. $J_0 = E_{AFM} - E_{FM}$ [4]. This simple approach takes into account both localized and conduction electrons contributions to the exchange interactions [20]. Table I shows exchange interactions with and without replacing Gd sites by Lu and La atoms. The exchange interactions substantially decrease when the Gd_1 site is substituted either by Lu or La in both structures of Gd_5Ge_4. When the Gd_2 and Gd_3 sites are substituted by Lu or La, the effect is much smaller despite a fourfold increase in the overall concentration of the nonmagnetic substitute. Hence, the Gd_1 position is particularly important in establishing the ferromagnetism of Gd_5Ge_4.

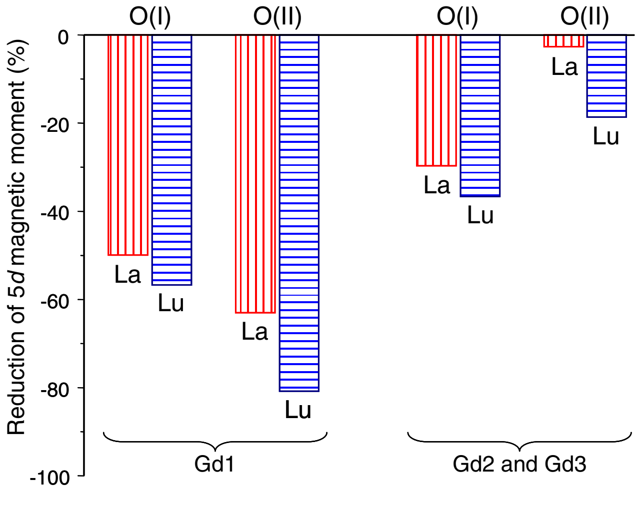

FIG. 2 (color online). The calculated reduction of the magnetic moments of the conduction electrons as a result of substituting different Gd atoms sites with La and Lu in two polymorphs of Gd_5Ge_4.

In order to validate the theoretical prediction of the critical role played by the Gd_1 site in the magnetism of Gd_5Ge_4, three samples were prepared and investigated: $(Gd_{1-x}La_x)_5Ge_4$ with $x = 0.05$, and $(Gd_{1-x}Lu_x)_5Ge_4$ with $x = 0.05$ and $x = 0.025$. A single crystal x-ray diffraction study of their crystal structures using four specimens of each compound showed that La and Lu do indeed substitute for Gd. While La is located almost exclusively in the Gd_2 position, Lu atoms selectively occupy the Gd_1 position (13% of Lu in the 4c site) with some filling the Gd_3 site (5% of Lu in the 8d site).

In concert with theory, even a tiny replacement of Gd_1 with Lu has an enormous effect on the magnetic and structural properties when compared with the parent Gd_5Ge_4 compound. Isothermal magnetization data shown in Fig. 3(a) reveal that the ground state of $(Gd_{0.975}Lu_{0.025})_5Ge_4$ is AFM, but at 20 K the AFM → FM transition occurs around 50 kOe compared to 16 kOe in pure Gd_5Ge_4; the critical magnetic field at 2 K becomes close to 70 kOe, compared to a 20 kOe field in the parent compound. Moreover, unlike in Gd_5Ge_4, the AFM-FM transition in $(Gd_{0.975}Lu_{0.025})_5Ge_4$ is fully reversible. The $(Gd_{0.95}Lu_{0.05})_5Ge_4$ alloy remains AFM in much higher magnetic fields (>70 kOe, Fig. 3(b)]. Here, the $M(H)$ data show only the beginning of a weak metamagnetic process above 50 kOe at 20 K, but not at 2 K. There is little evidence of a field-induced first-order phase transition, indicating that as little as 5% Lu substitution suppresses both the ferromagnetism and the magnetostructural transition in this system.

In contrast, magnetism of $(Gd_{0.95}La_{0.05})_5Ge_4$, where La substitutes for Gd_2, remains nearly identical to that of Gd_5Ge_4 [Fig. 3(c)]. The $M(H)$ data indicate a first-order transition in magnetic fields as low as 16–20 kOe at 2 and 30 K. Furthermore, the irreversible behavior at 2 K is similar to that of the parent compound.

Note that the observed effects are not related to volume changes due to chemical substitutions. First, these substi-

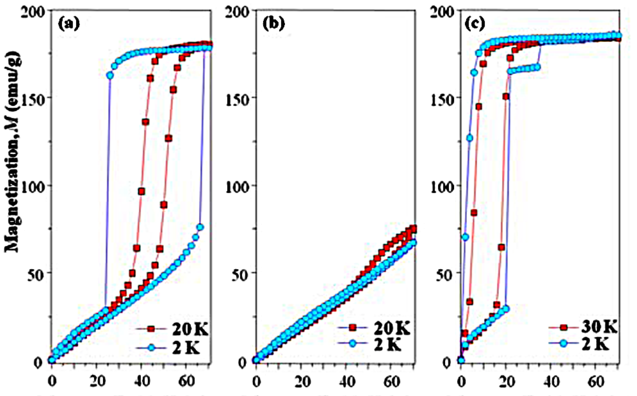

FIG. 3 (color online). The magnetization as a function of the applied magnetic field at selected temperatures for (a) $(Gd_{0.975}Lu_{0.025})_5Ge_4$, (b) $(Gd_{0.95}Lu_{0.05})_5Ge_4$, (c) $(Gd_{0.95}La_{0.05})_5Ge_4$ alloys.

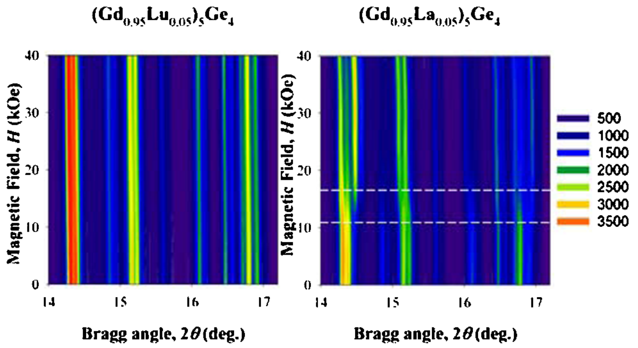

FIG. 4 (color online). The x-ray powder diffraction patterns of $(Gd_{0.95}Lu_{0.05})_5Ge_4$ (left) and $(Gd_{0.95}La_{0.05})_5Ge_4$ (right) collected isothermally in varying magnetic fields at 15 K.

tutions are at impurity levels, and phase volume changes remain small, especially for the $(Gd_{0.975}Lu_{0.025})_5Ge_4$ sample. Second, volume reduction actually promotes ferromagnetism in Gd_5Ge_4 [9] and in related $Gd_5(Ge_{1-x}Si_x)_4$ alloys [30], whereas the Lu substitution (Lu is smaller than Gd) has completely the opposite effect. Thus, nonmagnetic substitution on the Gd_1 site has a far greater effect than the reduction of the unit cell volume. The expansion of the unit cell due to La substitution does not have an impact on the magnetic behavior because La does not occupy the Gd_1 site, which is critically important for ferromagnetism.

In order to compare the low-temperature structural properties of $(Gd_{0.95}La_{0.05})_5Ge_4$ and $(Gd_{0.95}Lu_{0.05})_5Ge_4$ with Gd_5Ge_4, x-ray powder diffraction experiments in applied magnetic fields up to 40 kOe at temperatures from 5 to 50 K were performed. The structural behaviors of these alloys correspond to their magnetic properties. The $(Gd_{0.95}Lu_{0.05})_5Ge_4$ phase retains its O(II)-type structure in all measured fields and temperatures, whereas the La-substituted compound undergoes magnetostructural transformation similar to Gd_5Ge_4 (Fig. 4). At 15 K the transition is irreversible, so the structure of $(Gd_{0.95}La_{0.05})_5Ge_4$ remains O(I) after the sample is isothermally demagnetized. This is an indication that the kinetic arrest observed in Gd_5Ge_4 [7] is also present in the La-substituted alloys but not in the Lu-substituted alloys [see Fig. 3(a)].

In summary, we show that in a complex compound a specific location in the structure may be critically responsible for a given fundamental property of a material. Being able to identify the key atomic position(s) is like knowing the role of a specific gene in the DNA sequence, as such ability may ultimately result in materials by design. Another important implication of this work is in the identification of the FM interslab [Gd_1-Ge_3-Ge_3-Gd_1] nanowires embedded in the AFM Gd_5Ge_4 matrix. Spin ordering spreads through the lattice using particular atomic chains playing a determining role in creating the FM order in a solid, in our case, in Gd_5Ge_4. Replacing even a few of the magnetic Gd atoms within this chain with the nonmagnetic Lu atoms leads to a catastrophic loss of ferromagnetism, while identically small substitutions of other Gd positions with nonmagnetic La have essentially no effect on the magnetostructural transition (though we expect a loss of ferromagnetism at larger La concentrations due to dilution effects).

This work was supported by the Office of Basic Energy Sciences, Materials Sciences and Engineering Division of the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-07CH11358 with Iowa State University of Science and Technology.

[1] J. D. Watson and F. H. C. Crick, Nature (London) **171**, 964 (1953).
[2] W. Kohn, Rev. Mod. Phys. **71**, 1253 (1999).
[3] K. Bechgaard *et al.*, Phys. Rev. Lett. **46**, 852 (1981).
[4] D. Paudyal, V. K. Pecharsky, and K. A. Gschneidner, Jr., J. Phys. Condens. Matter **20**, 235235 (2008).
[5] E. M. Levin *et al.*, Phys. Rev. B **64**, 235103 (2001).
[6] C. Magen *et al.*, J. Phys. Condens. Matter **15**, 2389 (2003).
[7] S. B. Roy *et al.*, Phys. Rev. B **74**, 012403 (2006).
[8] V. K. Pecharsky *et al.*, Phys. Rev. Lett. **91**, 197204 (2003).
[9] C. Magen *et al.*, Phys. Rev. Lett. **91**, 207202 (2003).
[10] W. Choe *et al.*, Phys. Rev. Lett. **84**, 4617 (2000).
[11] D. Haskel *et al.*, Phys. Rev. Lett. **98**, 247205 (2007).
[12] V. K. Pecharsky *et al.*, J. Solid State Chem. **171**, 57 (2003).
[13] V. K. Pecharsky and K. A. Gschneidner, Jr., Pure Appl. Chem. **79**, 1383 (2007) and references therein.
[14] Ya. Mudryk *et al.*, Phys. Rev. B **77**, 024408 (2008).
[15] P. H. Tobash and S. Bobev, J. Am. Chem. Soc. **128**, 3532 (2006).
[16] G. J. Miller, Chem. Soc. Rev. **35**, 799 (2006).
[17] O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984).
[18] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).
[19] B. N. Harmon *et al.*, J. Phys. Chem. Solids **56**, 1521 (1995).
[20] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys. Condens. Matter **9**, 767 (1997).
[21] Materials Preparation Center, Ames Laboratory of US DOE, Ames, IA, USA, www.mpc.ameslab.gov.
[22] A. P. Holm *et al.*, Rev. Sci. Instrum. **75**, 1081 (2004).
[23] K. Ahn *et al.*, Phys. Rev. B **72**, 054404 (2005).
[24] D. Paudyal *et al.*, Phys. Rev. B **75**, 094427 (2007).
[25] The total energy difference (-20.7 meV/Gd) between the AFM O(II) and FM O(I) Gd_5Ge_4 is the sum of -18.5 meV/Gd due to the purely O(II)-O(I) structural transformation, and -2.2 meV/Gd due to the magnetic AFM-FM transition. Even though the latter value exceeds ~ 0.1 meV/Gd estimated purely from the change of the $5d$ magnetic moment ($\sim 0.5\mu_B$) and the critical field (~ 30 kOe) required to stabilize the FM O(I) phase, it does not account for the effects of strain [26] (in this case magnetic field induced) that promotes the formation of the FM O(I) phase.
[26] J. D. Moore *et al.*, Adv. Mater. **21**, 3780 (2009).
[27] D. Paudyal, T. Saha-Dasgupta, and A. Mookerjee, J. Phys. Condens. Matter **16**, 2317 (2004).
[28] L. Tan *et al.*, Phys. Rev. B **71**, 214408 (2005).
[29] E. M. Levin *et al.*, Phys. Rev. B **69**, 144428 (2004).
[30] Y. C. Tseng *et al.*, Phys. Rev. B **76**, 014411 (2007).