Crystal structure, magnetic properties, and the magnetocaloric effect of Gd₅Rh₄ and GdRh

C.L. Wang  
*Iowa State University*

J.D. Zhou  
*Iowa State University*

Jun Li  
*Iowa State University, junliu@AMESlab.gov*

Yaroslav Mudryk  
*Iowa State University, slavkomk@AMESlab.gov*

Karl A. Gschneidner Jr.  
*Iowa State University, cagey@AMESlab.gov*

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Crystal structure, magnetic properties, and the magnetocaloric effect of Gd5Rh4 and GdRh

Abstract
The crystal structures of Gd5Rh4 and GdRh have been studied by powder and single crystal x-ray diffraction. The results show that Gd5Rh4 is isotypic with Pu5Rh4 and the bond length of the short Rh-Rh dimer is 2.943(4) Å. According to heat capacity measurements in zero magnetic field, the magnetic ordering temperature of Gd5Rh4 is 13 K, in agreement with magnetization measurements. Both the heat capacity peak shape and the positive slope of the Arrott plots at Curie temperature (TC) indicate the second-order nature of the magnetic transition. The temperature dependence of magnetization of Gd5Rh4 measured in 1 kOe applied field indicates noncollinear magnetic ordering that may change into nearly collinear ferromagnetic ordering by increasing the magnetic field. GdRh is ferromagnetic below TC = 22 K. Moderate magnetocaloric effects and relatively high refrigerant capacities are observed in Gd5Rh4 and GdRh.

Disciplines
Ceramic Materials | Materials Chemistry | Metallurgy | Other Chemistry | Physical Chemistry

Comments
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Authors
C.L. Wang, J.D. Zhou, Jun Li, Yaroslav Mudryk, Karl A. Gschneidner Jr., Y. Long, Volodymyr Smetana, Gordon J. Miller, and Vitalij K. Pecharsky

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Crystal structure, magnetic properties, and the magnetocaloric effect of Gd₅Rh₄ and GdRh

C. L. Wang, J. D. Zou, J. Liu, Y. Mudryk, K. A. Gschneidner, Jr., Y. Long, V. Smetana, G. J. Miller, and V. K. Pecharsky

1The Ames Laboratory, U.S. Department of Energy, Iowa State University, Ames, Iowa 50011-3020, USA
2School of Materials Science and Engineering, University of Science and Technology of Beijing, Beijing 100083, People’s Republic of China
3Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-2500, USA
4Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111, USA

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The crystal structures of Gd₅Rh₄ and GdRh have been studied by powder and single crystal x-ray diffraction. The results show that Gd₅Rh₄ is isotypic with Pu₅Rh₄ and the bond length of the short Rh-Rh dimer is 2.943(4) Å. According to heat capacity measurements in zero magnetic field, the magnetic ordering temperature of Gd₅Rh₄ is 13 K, in agreement with magnetization measurements. Both the heat capacity peak shape and the positive slope of the Arrott plots at Curie temperature (T_C) indicate the second-order nature of the magnetic transition. The temperature dependence of magnetization of Gd₅Rh₄ measured in 1 kOe applied field indicates noncollinear magnetic ordering that may change into nearly collinear ferromagnetic ordering by increasing the magnetic field. GdRh is ferromagnetic below T_C = 22 K. Moderate magnetocaloric effects and relatively high refrigerant capacities are observed in Gd₅Rh₄ and GdRh. © 2013 American Institute of Physics.

The compounds Gd₅(Si₁₋ₓGex)₄ have received considerable attention since the discovery of a giant magnetocaloric effect in Gd₅Si₄Ge₄. Soon after, giant magnetostriction and giant magnetoresistance were also found in the Gd₅(Si₁₋ₓGex)₄ compounds. In this family of compounds, the magnetoresponsive effects are intimately related to the peculiar crystal structure that is composed from two-dimensional slabs. The Si/Ge-Si/Ge interslab bonds, which can be broken and reformed by changing temperature, pressure, magnetic field, and chemical composition, have a strong influence on the magnetic properties of all Gd₅(Si₁₋ₓGex)₄ compounds.

So far, the Gd₅T₄ systems (T = Si, Ge, Sn, Pb, In, Ga, Sb) have been studied at various depths, especially the silicides and germanides. Rhodium, a transition metal, when combined with gadolinium, forms the compound Gd₅Rh₄ which has the Gd₅Si₄-type structure (space group Pnma). However, the magnetic properties of Gd₅Rh₄ are, as yet, unreported. GdRh, which has the Gd₅Si₄-type structure (space group Pnma) has been studied at various depths, especially the silicides and germanides. However, Gd₅Rh₄ and GdRh were prepared by arc-melting the constituents in an argon atmosphere. Elemental Gd, with purity exceeding 99.9 wt. % with respect to all elements in the Periodic Table, was prepared by the Materials Preparation Center of the Ames Laboratory, and Rh metal, with purity of 99.99 wt. %, was purchased from a commercial vendor.

A Gd₅Rh₄ ingot was annealed in an evacuated silica tube at 1273 K for 7 days, and then quenched in an ice-water slurry. Phase analysis was performed by collecting the x-ray powder diffraction patterns, at room temperature on a PANalytical X’Pert Pro diffractometer using Cu Kα₁ radiation. A bulk GdRh sample was used for XRD due to its high ductility. The resulting XRD patterns were refined by the Rietveld method using the fullprof software. Magnetic properties were measured by using a superconducting quantum interference device (SQUID, MPMS-XL7) magnetometer from Quantum Design Inc. The zero-field heat capacity was measured in a physical properties measurement system (PPMS) from Quantum Design Inc.

A single crystal of Gd₅Rh₄ ∼ 0.10 × 0.08 × 0.06 mm³ was extracted from the annealed sample and used for the crystal structure determination. It was mounted on a Bruker APEX CCD single crystal diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation. Room temperature intensity data were collected in an o scans mode over 2θ = 5°–57° with exposure times of 10 s per frame. The reflections in the dataset were consistent with orthorhombic symmetry. Data integration, Lorentz polarization, and other corrections were completed by the SAINT subprogram included in the SMART software package. An empirical absorption correction was performed using the subprogram SADABS. The starting atomic parameters derived via direct methods and the program sir 97 (Ref. 16) were...
The zero-field-cooled-heating (ZFC) and field-cooled-cooling (FCC) magnetization curves of Gd₅Rh₄ measured in different magnetic fields are shown in Fig. 2. The cusp observed in ZFC and FCC curves in 1 kOe magnetic field at 14 K indicates the existence of weak aniferromagnetic interactions at low temperature. However, when the magnetic field is larger than 10 kOe, the ZFC and FCC curves exhibit a ferromagnetic-like ordering. The fully reversible ZFC and FCC curves at the transition temperature indicate a second-order transition, which is consistent with the “λ” type anomaly of the heat capacity data (not shown here) at 13 K in zero magnetic field and the positive slope of the Arrott plot shown in Fig. 3(c). The paramagnetic Curie temperature and effective magnetic moment calculated from the inverse susceptibility fitting of the 10 kOe ZFC magnetization curve from 100 K to 250 K (not shown here) are, respectively, 24 K and 7.84 μB/Gd atom (close to the theoretical value of 7.94 μB for the free Gd³⁺ ion). The positive paramagnetic Curie temperature of Gd₅Rh₄ indicates dominant ferromagnetic interactions, which is similar with the Gd₅T₄ (T = Si, Ge) compounds. The magnetization of Gd₅Rh₄ is far from saturation in 50 kOe field, as shown in Fig. 3(a), indicating that even in 50 kOe the ferromagnetic order is not fully collinear.

The inset of Fig. 2 shows a magnetic transition of GdRh from a ferromagnetic to paramagnetic state at 22 K in 100 Oe magnetic field. The absence of hysteresis in the magnetization curves at the Curie temperature indicates a second-order transition, which agrees with the earlier report of the “λ” type anomaly in the heat capacity and the positive slope of the Arrott plot shown in Fig. 3(d).

The entropy change ΔS(T, H) of Gd₅Rh₄ and GdRh have been calculated from the isothermal magnetization curves using the Maxwell relation

\[ ΔS(T, H) = \mu_H \left( \frac{∂M}{∂T} \right)_{µ_H} H. \]

The maximum entropy changes of Gd₅Rh₄ and GdRh, shown in Fig. 4, are 14 J/kg·K (at 16 K and 50 kOe) and 22 J/kg·K (at 24 K and 50 kOe), respectively. The relative cooling power (RCP) was estimated using the following equation

\[ RCP = -\Delta S_{\text{max}} \times \delta T_{\text{FWHM}} / H, \]

where \( \Delta S_{\text{max}} \) is the full width at half maximum of \( |ΔS| \) vs. \( T \) curve. The RCPs of Gd₅Rh₄ and GdRh for a magnetic field change of 0-50 kOe are 374 J/kg and 534 J/kg, respectively.
The crystal structures of Gd$_5$Rh$_4$ (Pu$_5$Rh$_4$-type) and GdRh (CsCl-type) have been confirmed by means of x-ray single crystal and powder diffraction. The $M(T)$ curves of Gd$_5$Rh$_4$ indicate the existence of a weak antiferromagnetic interaction in the ground state which can be changed to a predominantly ferromagnetic interaction by increasing magnetic field, although the magnetization curve does not saturate at 5 K in a 50 kOe field. The magnetic transitions in Gd$_5$Rh$_4$ and GdRh at 13 K and 22 K, respectively, have second-order character. Both Gd$_5$Rh$_4$ and GdRh have moderate magnetocaloric effects ($\Delta S_{\text{max}} = 14$ J/kg K and 22 J/kg K for $\Delta H = 50$ kOe, respectively). The former is significantly smaller than that of ErAl$_2$ (37 J/kg K, $T_C = 13.6$ K), which may be due to the antiferromagnetic interaction in Gd$_5$Rh$_4$. The GdRh value, however, is comparable with that of DyNi$_2$ (21 J/kg K, $T_C = 20.5$ K).

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[References]