Preparation, crystal structure, magnetic and magnetothermal properties of $(Gd_xR_{5-x})Si_4$, where R=Pr and Tb, alloys

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The series of alloys $(Gd_xTb_{5-x})Si_4$ $(x=0,2.5,3,3.5,4,4.5,5)$ and $(Gd_xPr_{5-x})Si_4$ $(x=4,4.25,4.5)$ have been prepared. Their room temperature crystal structure has been established, and dc magnetization and ac magnetic susceptibility have been measured in the temperature range from 4.2 to 550 K and in dc magnetic fields up to 50 kOe. The magnetocaloric effect has been calculated from the magnetization data and, for one of the alloys, from the heat capacity data. The magnetocaloric effect values from the two different measurements are in excellent agreement. The $(Gd_xTb_{5-x})Si_4$ alloys exhibit magnetocaloric effects in low magnetic fields (<20 kOe) comparable to that of Gd metal and, therefore, they represent a new class of promising magnetic refrigerant materials. [DOI: 10.1063/1.1335821]

I. INTRODUCTION

Recent advances in a laboratory scale magnetic refrigeration[1] indicate that it is likely to become the technology for the near room temperature applications offering considerable environmental benefits by eliminating ozone depleting, greenhouse, or hazardous gas/liquid refrigerants and, potentially, saving as much as 30% in operating energy costs. Just like the gas/liquid refrigerant in a conventional vapor compression system, a solid magnetic refrigerant material is an essential part of the magnetic refrigerator. Therefore, the discovery of better working substances suitable for use in magnetic refrigerators is important for the improvement of their performance. Recently, a giant magnetocaloric effect (MCE) was discovered in $Gd_5(Si_xGe_{1-x})_4$ alloys, where $x\leqslant 0.5$.[2,3] The giant MCE is brought about by the first order magnetic/crystallographic phase transition near the respective Curie temperatures. The Curie temperature is strongly dependent on the alloy composition and its first order nature is preserved even in high magnetic fields. The $Gd_5(Si_xGe_{1-x})_4$ alloys with $x>0.5$ do not exhibit the giant MCE, but they retain quite large values of the MCE and, most importantly, order magnetically above the ordering temperature of pure Gd metal maintaining good magnetocaloric properties between ~290 and ~340 K.[2]

The magnetic, electrical, and thermal properties of several binary R_5Si_4 alloys (where R is heavy lanthanide metal Gd, Tb, Dy, Ho, and Er) were studied in Refs. 4–8. Holtzberg *et al.*[4] found that upon cooling they order ferromagnetically with positive paramagnetic Curie temperatures Θ_p. The Curie temperatures T_C, effective magnetic moments p_{eff} and saturation magnetic moments μ_s, were also determined and are close to the theoretically expected values for the corresponding free R^{3+} ions.

Serdyuk *et al.*[6–8] measured electrical resistivity, heat capacity, and magnetization of Gd_5Si_4, Tb_5Si_4, Dy_5Si_4, and Ho_5Si_4 alloys. Anomalies near the Curie temperatures were observed in the temperature dependencies of both heat capacity and electrical resistivity of Gd_5Si_4, Tb_5Si_4, and Ho_5Si_4. The Curie temperature of Tb_5Si_4 was determined from heat capacity data to be $T_C=221.5$ K. It was shown that the character of the magnetic contributions to the electrical resistivity and the temperature dependencies of the heat capacity point towards the indirect RKKY-type exchange interaction between the lanthanide ions in these silicides.

Parviainen[5] measured the Curie temperatures of R_5Si_4 (R=Gd, Dy, Ho) alloys and their dependencies on the hydrostatic pressure up to 4 kbar using an inductance method. Curie temperatures were found to increase with pressure at the following rates: 0.29 K/kbar for Gd_5Si_4, 0.3 K/kbar for Dy_5Si_4, and 0.18 K/kbar for Ho_5Si_4.

Szade and Skorek[9] reported the high-temperature magnetic susceptibility and electrical resistivity of Gd_5Si_4. They show that Gd_5Si_4 follows Curie–Weiss behavior above ~700 K with $p_{\mathrm{eff}}=8.5\ \mu_B$ and $\Theta_p=343$ K. A small cusp in resistivity was observed at the Curie temperature, $T_C=336$ K. The resistivity of the silicide increases from ~30 $\mu\Omega$ cm at liquid helium temperature to ~330 $\mu\Omega$ cm at 400 K. However, Szade and Neumann[10] reported different results for Gd_5Si_4: $p_{\mathrm{eff}}=7.84\ \mu_B$ and $\Theta_p=369$ K, as determined from Curie–Weiss behavior of the inverse magnetic susceptibility above 700 K.

Elbicki *et al.*[11] studied a series of $(Gd_yM_{1-y})_5Si_4$ alloys, where M=La or Y, and y varies from 0.6 to 1.0. They found that both the Curie temperatures and the saturation magnetic moments are reduced with decreasing y. The addition of La or Y also decreases the sharpness of demagnetization near

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