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Magnetism of $R_2Ti_3Ge_4$ ($R=Sc, Gd, Tb, Dy, Ho, \text{ and } Er$) compounds

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(Presented on 8 January 2004)

Results of magnetization measurements down to 1.8 K on polycrystalline $R_2Ti_3Ge_4$ ($R=Sc, Gd, Tb, Dy, Ho, \text{ and } Er$) compounds of orthorhombic Sm_5Ge_4 -type (space group Pnma) are presented and discussed. $Gd_2Ti_3Ge_4$ is found to be a ferromagnet below 32 K while other $R_2Ti_3Ge_4$ compounds, with magnetic rare earths ($R=Tb, Dy, Ho, \text{ and } Er$), undergo a low temperature antiferromagnetic transition. The effective magnetic moment (μ_{eff}) values obtained from the Curie–Weiss paramagnetic susceptibility correspond to that of R^{3+} ions. Saturation of magnetization is not observed upto applied fields of 5.5 T at 1.8 K for all $R_2Ti_3Ge_4$ compounds except $Gd_2Ti_3Ge_4$, indicating the possible presence of crystal field effects. Electrical resistivity of these compounds is dominated by electron-phonon scattering above 20 K and signature of phonon and magnon drag effects are seen in the low temperature thermopower data. © 2004 American Institute of Physics. [DOI: 10.1063/1.1667836]

INTRODUCTION

Giant magnetocaloric effect at around room temperature has been observed in $Gd_5(Si_xGe_{1-x})_4$ alloys for $x=0.5$ composition near its ferromagnetic ordering temperature ($T_C=276$ K).^{1,2} With an aim to realize magnetic refrigeration near room temperature, new rare earth intermetallic compounds are being tailored and investigated by substituting at the Gd-site^{3–5} other rare earths or a transition metal⁶ in the above-mentioned alloys. Substitution of rare earths like Dy, Pr, and Ho at the Gd-site has always resulted in a reduction of the T_C . In this effort, a transition metal substitution, namely, titanium in an orthorhombic, (Sm_5Ge_4 -type) Gd_5Ge_4 alloy has resulted in the formation of stable $R_2Ti_3Ge_4$ intermetallic phase with $R=Sc, Gd, Tb, Dy, Ho, \text{ and } Er$. The choice of titanium metal was based on its excellent mechanical properties, which would render the material suitable for applications. In this work, the low temperature magnetic and electrical transport properties of $R_2Ti_3Ge_4$ ($R=Sc, Gd, Tb, Dy, Ho, \text{ and } Er$) are investigated and discussed.

EXPERIMENT

The $R_2Ti_3Ge_4$ ($R=Sc, Gd, Tb, Dy, Ho, \text{ and } Er$) compounds were prepared by electric arc melting under argon atmosphere starting from stoichiometric amounts of high purity constituent elements (Sc, Gd, Tb, Dy, Ho, and Er—99.9% pure, Ti and Ge—99.99% pure) followed by vacuum

annealing at 1100 K for eight days. Room temperature x-ray diffraction experiments confirmed the parent orthorhombic Sm_5Ge_4 -type structure (space group Pnma).⁷ The lattice parameters of the compounds vary in accordance with lanthanide contraction (Table I).

DC magnetization measurements were carried out from room temperature down to 1.8 K using a superconducting quantum interference device magnetometer (MPMS, Quantum Design, USA) up to applied fields of 5.5 T. DC electrical resistivity measurements were performed by standard four-probe technique in a Janis closed cycle refrigerator (CCR) in the temperature range of 15–300 K. The thermoelectric power was measured by employing conventional differential technique using copper as a reference material in CCR.

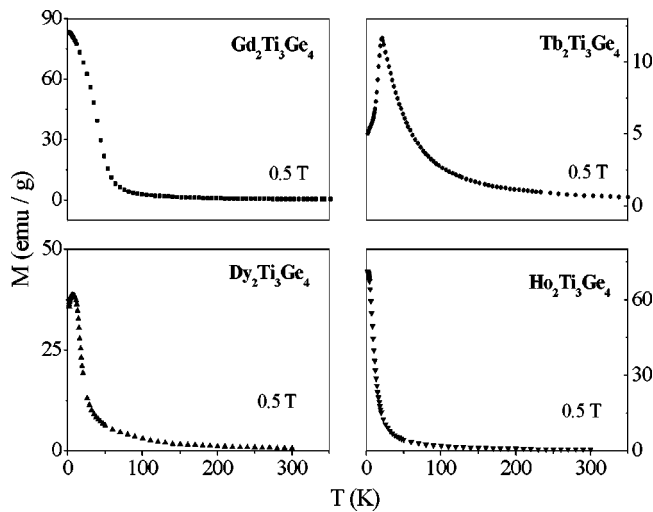
RESULTS AND DISCUSSIONS

The temperature (T) variation of magnetization (M) measured in applied fields of 0.5 mT and 0.5 T indicates that the $Gd_2Ti_3Ge_4$ compound undergoes a low temperature ferro-

TABLE I. Lattice parameters of $R_2Ti_3Ge_4$ ($R=Sc, Gd, Tb, Dy, Ho, \text{ and } Er$) compounds.

Compound	a (nm)	b (nm)	c (nm)
$Sc_2Ti_3Ge_4$	0.6791(2)	1.3107(3)	0.6924(2)
$Gd_2Ti_3Ge_4$	0.7042(1)	1.3494(2)	0.7186(4)
$Tb_2Ti_3Ge_4$	0.7016(1)	1.3455(2)	0.7157(1)
$Dy_2Ti_3Ge_4$	0.6987(1)	1.3409(2)	0.7122(1)
$Ho_2Ti_3Ge_4$	0.6981(1)	1.3400(2)	0.7117(1)
$Er_2Ti_3Ge_4$	0.6962(1)	1.3367(2)	0.7099(1)

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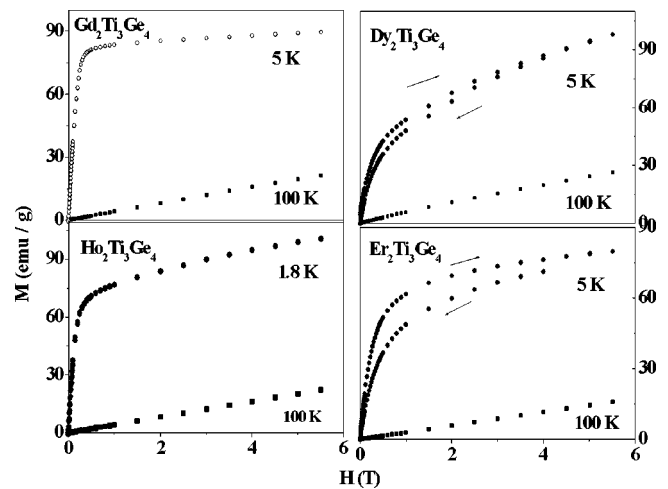
FIG. 1. Plot of $M(T)$ for $R_2Ti_3Ge_4$ ($R = Gd, Tb, Dy, \text{ and } Ho$) compounds.

magnetic transition at 32 K whereas all other magnetic rare earth containing samples of $R_2Ti_3Ge_4$ series ($R = Tb, Dy, \text{ and } Ho$) were found to have a paramagnetic to antiferromagnetic phase change (Fig. 1). In the case of $Er_2Ti_3Ge_4$ compound, no antiferromagnetic peak like feature was observed in M down to 1.8 K but the compound shows a tendency to order magnetically in a low applied field of 0.5 mT. The suppression of Néel temperature with the application of larger magnetic field is consistent with the antiferromagnetic nature of $R_2Ti_3Ge_4$ ($R = Tb, Dy, \text{ and } Ho$) compounds. The $Sc_2Ti_3Ge_4$ compound is found to be nonmagnetic down to 1.8 K. The effective magnetic moments calculated from the high temperature Curie–Weiss fit to the susceptibility, compare well with the free ion moments of corresponding rare earths. The ordering temperatures (T_C or T_N), paramagnetic Curie temperature θ_p , effective magnetic moment μ_{eff} , and magnetization values in 5.5 T applied field in the ordered state, $M(5.5 \text{ T})$ are presented in Table II.

The field (H) dependence of magnetization has been studied and the M - H isotherms have been obtained at 5 and 100 K up to the field of 5.5 T (Fig. 2). For Tb, Ho, and Er compounds, to understand the behavior of $M(H)$ in the magnetically ordered state, measurements were carried out at 1.8 K (at $T < T_N$). In the paramagnetic state, magnetization varies linearly with applied field. The isotherms of $R_2Ti_3Ge_4$ ($R = Tb, Dy, Ho, \text{ and } Er$) compounds at low temperatures are quite complex for an antiferromagnet. The low temperature magnetization of $Dy_2Ti_3Ge_4$ and $Er_2Ti_3Ge_4$ compounds

TABLE II. Magnetic properties of $R_2Ti_3Ge_4$ ($R = Gd, Tb, Dy, Ho, \text{ and } Er$) compounds.

Compound	$T_{C,N}$ (K)	θ_p (K)	μ_{eff} (μ_B/R^{3+})	$M(5.5 \text{ T}, 5 \text{ K})$ (μ_B/R^{3+})
$Gd_2Ti_3Ge_4$	32	2.7	7.57	6.03
$Tb_2Ti_3Ge_4$	18	-8.5	9.17	5.28 ^a
$Dy_2Ti_3Ge_4$	8	-4.8	9.52	6.67
$Ho_2Ti_3Ge_4$	8	-18.4	9.52	6.90 ^a
$Er_2Ti_3Ge_4$	—	-4.3	8.68	5.50

^aObtained at 2 K.FIG. 2. Plot of M vs H for $R_2Ti_3Ge_4$ ($R = Gd, Dy, Ho, \text{ and } Er$) compounds.

shows considerably large hysteresis. The magnetic structure of these compounds is most likely a complex canted one as in parent R_5X_4 -type compounds, with both ferro- and antiferromagnetic correlations.

Magnetization saturates only for $Gd_2Ti_3Ge_4$ compound in 5.5 T field at 5 K, but not for other compounds. The magnetic moment value in the ordered state (Table II) is less than the free-ion moment, suggesting the existence of anisotropy due to crystal field effects. Also a significant deviation from Curie–Weiss behavior in susceptibility was observed in the case of the $Tb_2Ti_3Ge_4$ compound at around 50 K. In these compounds titanium does not carry a magnetic moment as in the case of $R_2Ti_3Si_4$, $RTiSi$, and $RTiGe$ compounds.^{6,8–10}

The electrical resistivity ρ of all the $R_2Ti_3Ge_4$ compounds investigated here is metallic and is of the order of few tens of $\mu\Omega \text{ cm}$. Resistivity of these compounds follows the equation of the form given below

$$\rho(T) = \rho_0 + A \int_0^{\theta_D/T} x^5 dx / (e^x - 1)(1 - e^{-x}), \quad (1)$$

where ρ_0 is the residual resistivity and the second term is the conventional Bloch–Grüneisen expression for the electron–phonon scattering. Typical slope change in resistivity near T_C is observed for $Gd_2Ti_3Ge_4$ (Fig. 3). For the other compounds, the magnetic ordering temperatures being low, their signature in electrical resistivity might be explicit at much lower temperatures. From the fit to the resistivity curve, the Debye temperature, θ_D , values are calculated. The resistivity values at typical temperatures and also the fit parameters are listed in Table III. The resistivity at room temperature is more for Tb- compound and it decreases systematically for heavier rare earth containing compounds.

The thermoelectric power (S) of the $R_2Ti_3Ge_4$ compounds is negative at room temperature and shows a peak feature at low temperatures (Fig. 4). The S of Gd-compound alone shows a double hump in the neighborhood of T_C . The low temperature thermopower behavior of magnetic rare earth containing $R_2Ti_3Ge_4$ ($R = Gd, Tb, Dy, Ho, \text{ and } Er$) compounds must be the result of a combined effect of mag-

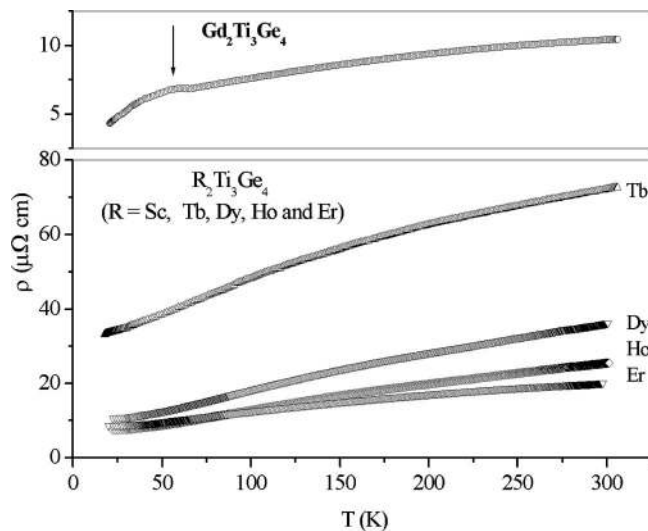


FIG. 3. Plot of resistivity (ρ) vs T for $R_2Ti_3Ge_4$ ($R = Sc, Gd, Tb, Dy, Ho,$ and Er) compounds.

non and phonon drag as the peak feature in S is not pronounced in the nonmagnetic analog, $Sc_2Ti_3Ge_4$.

In conclusion, Sm_5Ge_4 -type orthorhombic, $R_2Ti_3Ge_4$ rare earth intermetallic phases have been synthesized and characterized. The $R_2Ti_3Ge_4$ ($R = Tb, Dy,$ and Ho) compounds are found to have antiferromagnetic ground state at low temperatures whereas $Gd_2Ti_3Ge_4$ is ferromagnetic below 32 K. Titanium does not carry a magnetic moment in these samples. Reduced magnetic moment value in the ordered state of $R_2Ti_3Ge_4$ ($R = Tb, Dy, Ho,$ and Er) suggests the presence of anisotropy due to crystal field effects. Electrical resistivity is dominated by electron-phonon scattering

TABLE III. Electrical resistivity values and the parameters from fit to Eq. (1).

Compound	ρ (300 K) ($\mu\Omega$ cm)	ρ (20 K) ($\mu\Omega$ cm)	ρ_0 ($\mu\Omega$ cm)	A	θ_D (K)
$Sc_2Ti_3Ge_4$	67	46	46	78	222
$Gd_2Ti_3Ge_4$	10	4	4	28	304
$Tb_2Ti_3Ge_4$	72	33	33	127	163
$Dy_2Ti_3Ge_4$	36	10	10	103	232
$Ho_2Ti_3Ge_4$	25	7	7	73	231
$Er_2Ti_3Ge_4$	20	8	8	49	216

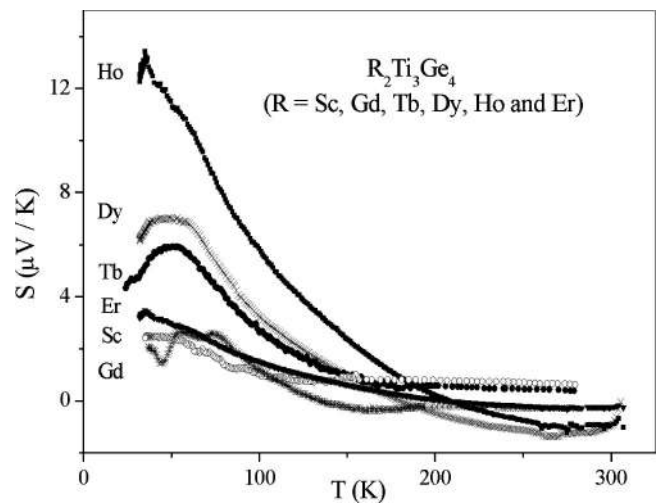


FIG. 4. Plot of thermopower (S) vs T for $R_2Ti_3Ge_4$ ($R = Sc, Gd, Tb, Dy, Ho,$ and Er) compounds.

above 20 K and the signature of the ferromagnetic transition is visible in the $\rho(T)$ for $Gd_2Ti_3Ge_4$ whereas phonon and magnon drag effects determine the low temperature thermopower behavior. Low temperature neutron diffraction measurements on these compounds are in progress.

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