Electrical transport and magnetism in Mo-substituted R2Ti3Ge4 (R = Tb,Er) compounds

R. Nirmala, K. Hima Nagamanasa, P. A. Bhobe, Jagat Lamsal, and A. K. Nigam

Citation: J. Appl. Phys. **105**, 07A914 (2009); doi: 10.1063/1.3065977
View online: http://dx.doi.org/10.1063/1.3065977
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v105/i7
Published by the American Institute of Physics.

Electrical transport and magnetism in Mo-substituted $R_2Ti_3Ge_4$ (R=Tb,Er) compounds

R. Nirmala,[1] K. Hima Nagamanasa,[2] P. A. Bhobe,[3] Jagat Lamsal,[4] and A. K. Nigam[3,a)]
[1]*Department of Physics, Indian Institute of Technology Madras, Chennai 600 036, India*
[2]*School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067, India*
[3]*Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai 400 005, India*
[4]*Department of Physics and Astronomy, University of Missouri-Columbia, Columbia, Missouri 65211, USA*

(Presented 13 November 2008; received 23 September 2008; accepted 31 October 2008; published online 9 February 2009)

The effect of Mo substitution at Ti site of orthorhombic Sm_5Ge_4-type $R_2Ti_3Ge_4$ compounds on the magnetic and electrical transport properties has been studied. The $Tb_2Ti_{3-x}Mo_xGe_4$ (x=0.3,0.75) and $Er_2Ti_{2.7}Mo_{0.3}Ge_4$ compounds have been synthesized and it is found that these compounds retain parent crystal structure at room temperature (space group *Pnma*, No. 62). Mo substitution decreases the antiferromagnetic ordering temperature (T_N) of $Tb_2Ti_3Ge_4$ compound from ~18 to ~13 and ~10 K, respectively, for x=0.3 and 0.75. The $Er_2Ti_{2.7}Mo_{0.3}Ge_4$ compound shows a tendency to order at ~2 K, whereas the parent $Er_2Ti_3Ge_4$ is magnetically ordered at 3 K. Magnetization versus field data of $Tb_2Ti_{3-x}Mo_xGe_4$ (x=0.3,0.75) reveal soft ferromagnetic nature. The metamagnetic transition that is present in parent $Tb_2Ti_3Ge_4$ is found to disappear with Mo substitution. Magnetization value reaches ~6.2μ_B/Tb^{3+} at 2 K in fields of 8 T, indicating incomplete ferromagnetic ordering with or without an antiferromagnetic component. Electrical resistivity of the Tb-based compounds has a linear variation with temperature from 300 to ~50 K and shows a prominent slope change at temperatures much above T_N, supporting the presence of competing short range ferromagnetic interactions. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3065977]

I. INTRODUCTION

Rare earth intermetallic compounds of orthorhombic Sm_5Ge_4-type layered crystal structure have received a great deal of attention in the past decade because some of these compounds such as $Gd_5(Si_xGe_{1-x})_4$ display interesting magnetic and magnetocaloric properties in the temperature span of 20–280 K.[1–3] Large magnetocaloric effect (MCE) is observed in the vicinity of the magnetic transition, which is often coupled to the lattice degree of freedom as well. Hence these materials are considered as promising candidates for energy saving and ecofriendly magnetic refrigeration. Recently isostructural $R_2Ti_3Ge_4$ (R=Gd,Tb,Er) compounds were found to exhibit large MCE at low temperatures.[4] Since R-R distance within the layer and across the layer and the covalent bonds of p-elements play a vital role in determining the ground state magnetic properties of Sm_5Ge_4-type compounds through the underlying Ruderman–Kittel–Kasuya–Yoshida exchange interaction, we aim to study the effect of Mo substitution at Ti site of $R_2Ti_3Ge_4$ (R=Tb,Er) compounds.

II. EXPERIMENTAL DETAILS

The $Tb_2Ti_{3-x}Mo_xGe_4$ (x=0.30,0.75) and $Er_2Ti_{2.7}Mo_{0.3}Ge_4$ compounds have been synthesized by arc melting under argon atmosphere starting from stoichiometric amounts of pure starting elements (Tb, Er 99.9% pure, Ti and Ge 99.999% pure, Cerac, Inc., USA). The samples were remelted several times to ensure the homogeneity and these were characterized by powder x-ray diffraction experiments at room temperature. The sample composition was verified by energy dispersive x-ray analysis. Magnetization measurements were carried out in the temperature range of 2–300 K using commercial magnetometers (magnetic properties measurement system superconducting quantum interference device, Quantum Design, USA and vibrating-sample magnetometer, Oxford, Inc.) in various applied fields. Electrical resistivity was measured by linear four probe method on a bar shaped sample in the temperature range of 2–300 K using physical property measurement system, Quantum Design, USA.

III. RESULTS AND DISCUSSION

Rietveld analysis of room temperature x-ray diffraction data showed that these compounds crystallize in orthorhombic Sm_5Ge_4-type (space group *Pnma*, No. 62) structure as the parent $R_2Ti_3Ge_4$ (R=Tb,Er) compounds.[5] The unit cell volume is found to decrease with Mo substitution (Table I).

Magnetization versus temperature of $Tb_2Ti_{3-x}Mo_xGe_4$ (x=0.30,0.75) and $Er_2Ti_{2.7}Mo_{0.3}Ge_4$ compounds in applied field of 0.5 T is illustrated in Fig. 1. The temperature dependence of zero-field cooled (ZFC) and field-cooled (FC) magnetizations of $Tb_2Ti_{3-x}Mo_xGe_4$ (x=0.30,0.75) compounds in 10 mT applied field is shown as inset in Fig. 1. The Tb-based compounds show a cusp in low field magnetization, which is a characteristic of an antiferromagnetic transition. However,

a)Author to whom correspondence should be addressed. Electronic mail: aknm@tifr.res.in.

TABLE I. Lattice parameters a, b, and c and unit cell volume V of $Tb_2Ti_{3-x}Mo_xGe_4$ (x=0.30,0.75) and $Er_2Ti_{2.7}Mo_{0.3}Ge_4$ compounds. Data for parent $R_2Ti_3Ge_4$ (R=Tb,Er) compounds are also given for Ref. 5.

Compound	Structure type	a (Å)	b (Å)	c (Å)	Volume (Å^3)
$Tb_2Ti_3Ge_4$	Sm_5Ge_4	7.019	13.457	7.156	675.92
$Tb_2Ti_{2.7}Mo_{0.3}Ge_4$	Sm_5Ge_4	6.992	13.413	7.124	668.115
$Tb_2Ti_{2.25}Mo_{0.75}Ge_4$	Sm_5Ge_4	7.026	13.364	7.09	665.718
$Er_2Ti_3Ge_4$	Sm_5Ge_4	6.962	13.367	7.099	660.63
$Er_2Ti_{2.7}Mo_{0.3}Ge_4$	Sm_5Ge_4	6.938	13.35	7.087	656.758

a ferromagneticlike increase in magnetization was seen in applied field of 0.5 T. The antiferromagnetic ordering temperature (T_N) of parent $Tb_2Ti_3Ge_4$ compound from ~18 K (Refs. 4 and 6) is decreased to ~13 and ~10 K, respectively, for x=0.3 and 0.75 Mo substitution [Figs. 1(a) and 1(b)]. The $Er_2Ti_{2.7}Mo_{0.3}Ge_4$ compound has a tendency to magnetically order at about 2 K [Fig. 1(c)], which is also the limiting temperature of the instrument. The parent $Er_2Ti_3Ge_4$ has been found to be magnetically ordered at 3 K by means of heat capacity experiments.[4]

The paramagnetic susceptibility follows the Curie–Weiss law. The ZFC-FC curves branch at a temperature closer to the magnetic ordering temperature with a strong deviation from Curie–Weiss behavior much above T_N. The difference between ZFC and FC magnetization data and positive paramagnetic Curie temperature indicates the presence of competing magnetic interactions.

Magnetization versus field data of $Tb_2Ti_{3-x}Mo_xGe_4$ (x =0.3,0.75) reveals soft ferromagnetic nature (Fig. 2). The metamagnetic transition that is present in parent $Tb_2Ti_3Ge_4$ in a critical field of about 0.5 T is found to disappear with Mo substitution. Magnetization value reaches ~$6.2\mu_B/Tb^{3+}$ at 2 K in fields of 8 T, indicating incomplete ferromagnetic ordering with or without an antiferromagnetic component. Crystal field effects are also likely to influence the ordered state magnetic moment values. It is of relevance to recollect that the parent $Tb_2Ti_3Ge_4$ compound, which undergoes field-induced magnetic transition at 2.5 K, gives rise to a satura-

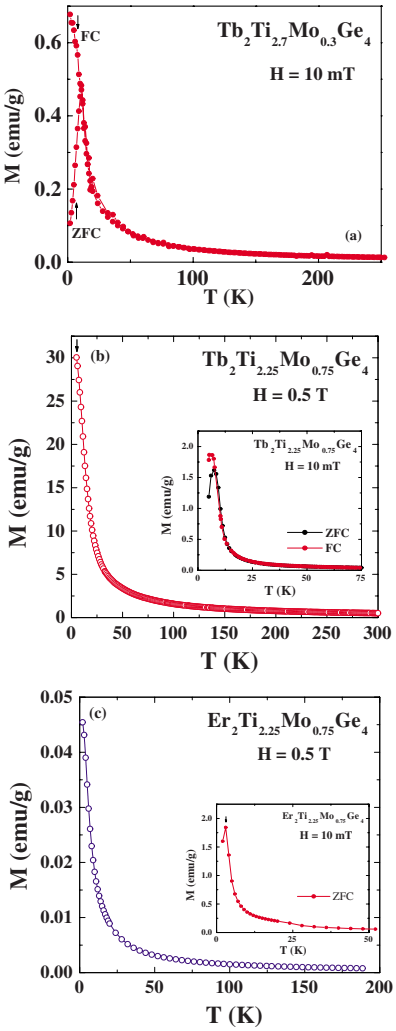

FIG. 1. (Color online) Temperature dependence of magnetization of $Tb_2Ti_{3-x}Mo_xGe_4$ (x=0.30,0.75) and $Er_2Ti_{2.7}Mo_{0.3}Ge_4$ compounds.

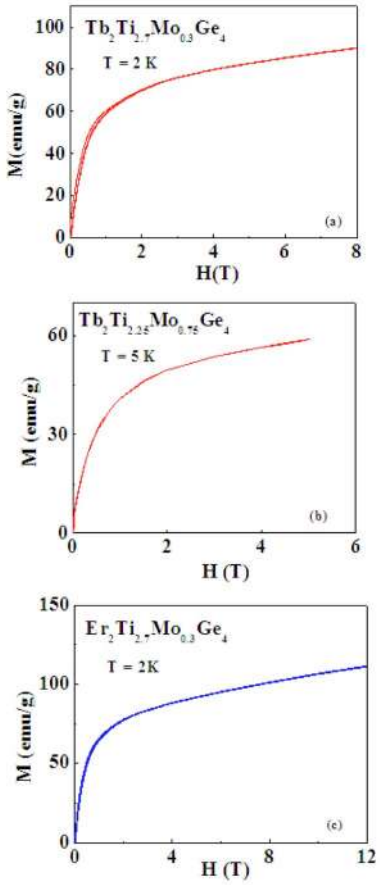

FIG. 2. (Color online) Magnetization vs field isotherm in the ordered state of $Tb_2Ti_{3-x}Mo_xGe_4$ (x=0.30,0.75) and $Er_2Ti_{2.7}Mo_{0.3}Ge_4$ compounds.

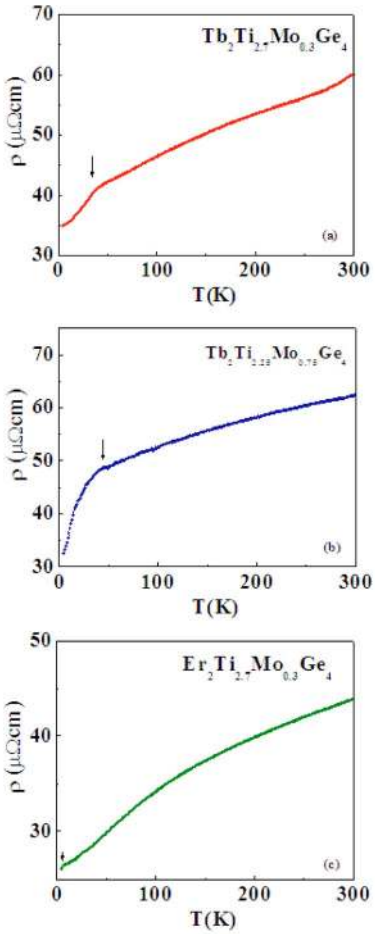

FIG. 3. (Color online) Temperature dependence of electrical resistivity of $Tb_2Ti_{3-x}Mo_xGe_4$ ($x=0.30,0.75$) and $Er_2Ti_{2.7}Mo_{0.3}Ge_4$ compounds.

tion magnetization of only $\sim 5.6\mu_B/Tb^{3+}$. Mo substitution has possibly increased the overall ferromagnetic interactions that prevail in the three dimensional lattice and hence resulting in positive paramagnetic Curie temperature values and soft ferromagnetic nature in applied fields.

Electrical resistivity is plotted as a function of temperature for the $Tb_2Ti_{3-x}Mo_xGe_4$ ($x=0.30,0.75$) and $Er_2Ti_{2.7}Mo_{0.3}Ge_4$ compounds in Fig. 3. Electrical resistivity of the Tb-based compounds has a linear variation with temperature from 300 to about 50 K. Electrical resistivity shows a prominent slope change at temperatures much above T_N, supporting the presence of competing short range ferromagnetic interactions. However, magnetoresistance is found to be positive and small in all these compounds.

In the case of isostructural material Gd_5Ge_4, low temperature x-ray diffraction experiments in the presence of applied magnetic field revealed that the sharp metamagnetic transition at low temperature is triggered by a structural change,[7] which also led to giant MCE. The low field Sm_5Ge_4-type structure has been found to transform into a high field Gd_5Si_4-type structure with a strengthening of interlayer Ge–Ge bonds. Thus the present work of substitution in $R_2Ti_3Ge_4$ compounds was aimed at enhancing the overall ferromagnetic interactions in the three-dimensional structure, which supports both ferromagnetic and antiferromagnetic components by achieving a crystal structure change as a function of temperature and field by tuning the intralayer and interlayer *R-R* bond distances, thus effectively regulating the exchange interactions. As evidenced by the magnetization and electrical transport studies, possibly the short-range ferromagnetic interactions are enhanced, as suggested by the increase in saturation magnetization value, demarcation from Curie–Weiss law just above T_N, and the deviation from linear behavior in electrical resistivity well above T_N, although the low field antiferromagnetic ordering temperature is slightly reduced from that of parent compounds. Heat capacity of the substituted compounds and MCE in these materials could give interesting results and these experiments are in progress.

IV. CONCLUSIONS

In summary, new polycrystalline, orthorhombic Sm_5Ge_4-type, $Tb_2Ti_{3-x}Mo_xGe_4$ ($x=0.30,0.75$) and $Er_2Ti_{2.7}Mo_{0.3}Ge_4$ compounds have been synthesized and characterized. These compounds undergo from room temperature paramagnetic to low temperature antiferromagnetic transition at temperatures less than 20 K. Electrical resistivity is linear in temperature with a slope change at temperatures much above T_N.

ACKNOWLEDGMENTS

The authors thank D. Buddhikot for his help during magnetic measurements, B. A. Chalke for EDAX analysis, and S. Venkatesh for help in arc melting some of the samples.

[1] V. K. Pecharsky and K. A. Gschneidner, Jr., Appl. Phys. Lett. **70**, 3299 (1997).
[2] V. Provenzano, A. J. Shapiro, and R. D. Shull, Nature (London) **429**, 853 (2004).
[3] E. Brück, J. Phys. D **38**, R381 (2005).
[4] R. Nirmala, D. C. Kundaliya, A. V. Morozkin, and S. K. Malik, J. Appl. Phys. **103**, 053905 (2008).
[5] A. V. Morozkin, Yu. D. Seropegin, V. K. Portnoy, A. V. Leonov, and I. A. Sviridov, J. Alloys Compd. **278**, L8 (1998).
[6] R. Nirmala, V. Sankaranarayanan, K. Sethupathi, G. Rangarajan, A. V. Morozkin, D. C. Kundaliya, and S. K. Malik, J. Appl. Phys. **95**, 7079 (2004).
[7] A. P. Holm, V. K. Pecharsky, K. A. Gschneidner, Jr., R. Rink, and M. N. Jirmanus, Rev. Sci. Instrum. **75**, 1081 (2004).