Second Order Magnetic Phase Transition in RCo_9Si_4 (R = Sm, Gd and Tb)

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Magnetization, resistivity and specific heat measurements were performed on the polycrystalline samples of the ternary compounds RCo_9Si_4 (R = Sm, Gd and Tb) in order to investigate the thermodynamic and transport properties. The low temperature results reveal the onset of ferromagnetic order at Curie temperatures T_c varying between 30 and 50 K for RCo_9Si_4 on going from Sm to Tb compounds. The electrical resistivities in the ordered state (below $T_C/2$) is in reasonable agreement with the quadratic temperature dependence expected from ferromagnetic spin waves. Thermodynamic and transport data of the ordered ternary compounds reveal a second order phase transition from paramagnetic to the magnetic ordered state which can clearly be derived from the kinks like anomalies in the resistivity data and the jump like anomalies in the specific heat measurements.

1. Introduction:

Among rare earth intermetallic compounds formed with *3d* transition metals, $LaCo_{13}$ is the one with the highest concentration of transition element and has a very large magnetization (130 emu/g at 300 K) and high magnetic transition temperature (T_C = 1318 K). Its magnetic moment is 1.56 μ_B per Co atom [1,2], but its magnetocrystalline anisotropy is low because of the cubic $NaZn_{13}$-type structure. Several groups tried to enhance the magnetocrystalline anisotropy of $LaCo_{13}$ based intermetallic compounds by elemental substitution on the Co site [2]. It has been observed that Si doping results in a degrading of their crystal symmetry from cubic $NaZn_{13}$ to tetragonal type structure, with a slight improvement of the magnetocrystalline anisotropy [3,4,5].

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In a search for new magnetic materials having potential for applications as high performance permanent magnets, the properties of true ternary RCo$_9$Si$_4$ compounds with a fully ordered crystal structure have attracted attention due to their interesting magnetic properties. They exhibit a spectrum of very interesting physical properties depending on the R atom [6-11]. The structure of RCo$_9$Si$_4$ is isotypic with the LaFe$_9$Si$_4$ structure [12], which represents an ordered tetragonal derivative of well known cubic NaZn$_{13}$ (cF112) type structure. The tetragonal structure of space group *I4/mcm* was determined for the first time by Bodak [13] for the partially disordered phase CeNi$_{8.5}$Si$_{4.5}$. Besides LaFe$_9$Si$_4$, crystallization in the completely ordered version was also found for RCo$_9$Si$_4$ phases with R = Pr and Nd [14], R = Nd [15] and R = Sm [16], Gd, Tb and Y [7], whilst for CeCo$_{8.5}$Si$_{4.5}$ studied by neutron diffraction [17] a random occupancy of Co/Si on one site was observed. Coexistence of disordered cubic and ordered or partially ordered tetragonal structure was reported in some RCo$_{13-x}$Si$_x$ systems.

Magnetic properties of RCo$_{13-x}$Si$_x$ series have been studied by Huang et al. [6]. They found that at low Si content, $1.5 < x < 2.0$, face-centered cubic (fcc) alloys are formed with high T_C which are strongly magnetic, while at high Si content, $3.5 < x < 4.5$, body-centered tetragonal (bct) formed which are weakly magnetic with T_C at or below room temperature.

Skolozdra et al. [7] reported some magnetic results on RCo$_9$Si$_4$ systems with R = Sm, Gd, Tb and Y. They observed a significantly higher T_C (~ 900 K) values, with rather small magnetic moments per Co atom (~ 0.4 μ_B), than those announced by Huang et al. [6] for RCo$_9$Si$_4$ systems with R = La, Pr, Nd, Gd, and Dy (T_C ~ 20-50 K). In our earlier investigations on RCo$_9$Si$_4$ systems, the compound with R = La is found to be a strongly exchange enhanced Pauli paramagnet and exhibits an itinerant electron metamagnetism [8]. On the other hand YCo$_9$Si$_4$ compound shows a weak itinerant ferromagnetism while CeCo$_9$Si$_4$ system exhibits intermediate valence with Ce being close to a non-magnetic tetravalent state [9,10]. Furthermore, the related isostructural RCo$_9$Si$_4$ with R = Pr and Nd are ferromagnetic with first-order type of magnetic phase transition at a relatively lower T_C [11].

In attempt to complete studies, magnetic ordering behaviours, thermodynamic and transport properties, on the other RCo$_9$Si$_4$ series, we investigate in the present work magnetization, ac susceptibility, electrical resistivity and specific heat for RCo$_9$Si$_4$ with R = Sm, Gd, and Tb compounds. One has to mention that formation of the CeNi$_{8.5}$Si$_{4.5}$-type bct phase does not occur in the alloys with heavy rare earth.

2. Experimental procedures:

Polycrystalline samples of ternary RCo$_9$Si$_4$ with R = Sm, Gd and Tb were synthesized on a water-cooled copper groove by high frequency induction melting under argon atmosphere. The starting materials are rare earth ingots (Sm, Gd and Tb) Strem chemicals, USA: 99.9 %, Germany: 99.9999 %), Cobalt ingots (Alfa Aesar, Germany: 99.999 %), and Silicon chips (Strem chemicals, USA: 99.9999 %). In order to obtain homogenous samples, the preparation was performed in two steps: First, Co and Si were melted together for four times. Second, rare earth and the precursor alloy CoSi were melted together. To ensure homogeneity, the buttons were broken and remelted for at least 4 times. The weight loss (1-2 %) due to the evaporation of silicon was determined by weighing the alloy after each remelting stage and compensated accordingly. The samples were wrapped into a Ta foil and then annealed at 1050 ºC for at least one week in evacuated quartz ampules. In order to obtain more information concerning the effect of the annealing temperature on the stoichiometric of the samples, two TbCo$_9$Si$_4$ samples were prepared (A and B) and annealed at two different annealing temperatures 1050 ºC and 1000 ºC, respectively.

The phase purity of the samples was checked at room temperature by means of X-ray powder diffraction (XRD) with Co-Kα_1 radiation (λ= 1.78890 Å). Complementary measurements of ac susceptibility in the temperature range 1.8-300 K were performed with a calibrated Lake Shore 7000 susceptometer in zero dc field with an applied ac field of amplitude up to 200 A/m at a frequency of 80 Hz. Magnetization data were taken by using a Cryogenic Instruments 6T superconducting quantum interference device (SQUID) magnetometer. The resistivities $\rho(T)$ were measured between 4.2 and 300 K using a standard four-point dc technique on samples of dimension 1 x 1 x 20 mm^3 cut by means of wire diamond saw. The specific heat results were obtained from 1.5 to 80 K with a quasi adiabatic step heating technique.

3. Results and discussion:

The XRD patterns of RCo$_9$Si$_4$ (R = Sm, Gd and Tb) are shown in Fig.(1). The reflection lines of the samples were indexed on the basis of the tetragonal lattice of LaFe$_9$Si$_4$ – type structure with space group I4/mcm [12] indicating that the samples of RCo$_9$Si$_4$ are essentially single phase. A very few weak extra lines indicate the presence of small amounts of secondary phases (mainly traces of Co$_2$Si). Precise lattice parameters were obtained with the method of least square refinement and are listed in Table (1). The decrease of lattice parameter is consistent with the larger ionic radii of Sm^{3+} and Gd^{3+} as compared to Tb^{3+}. The increase of lattice parameter of TbCo$_9$Si$_4$ sample (B) as

compared to sample (A) might be attributed to the disorder effect. The values obtained agree well with those reported in literature [6,7,13]. The phase purity and composition has been verified by electron microprobe investigation.

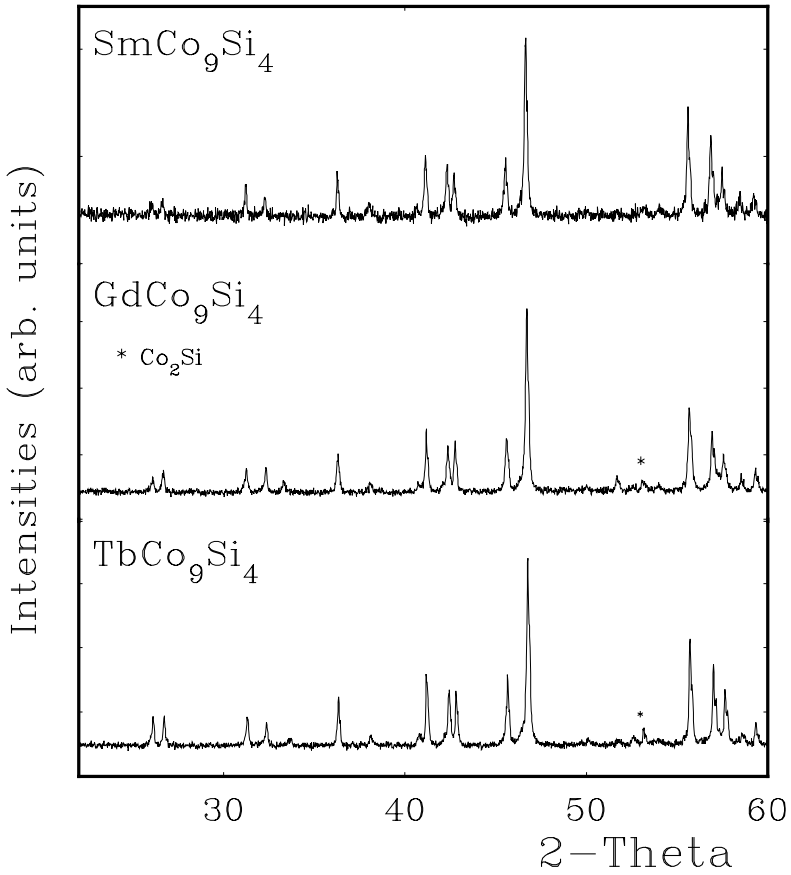

Fig. (1): X-ray diffraction patterns of the tetragonal type structure RCo$_9$Si$_4$ with R = Sm, Gd and Tb.

The temperature dependence of the ac magnetic susceptibilities $\chi(T)$ for RCo$_9$Si$_4$ with R = Sm, Gd and Tb, displayed in Fig. (2), shows sharp transitions at low temperatures. Such anomalies typically arise due to the transition from the paramagnetic to the ferromagnetic ordered state. The onset of ferromagnetic order at Curie temperatures T_C were obtained from a very sharp increase in the ac susceptibility data and found to vary from 30 to 50 K. The magnetic ordering temperatures of RCo$_9$Si$_4$ summarized in Table (1) being consistent with the values reported by Huang et al. [6]. However, these low temperature results

appear to disagree with the significantly higher T_C ~ 900 K reported by Skolozdra et al. [7] for RCo$_9$Si$_4$ with R = Sm, Gd and Tb, which may be attributed to a few percent of pure Co metal [6].

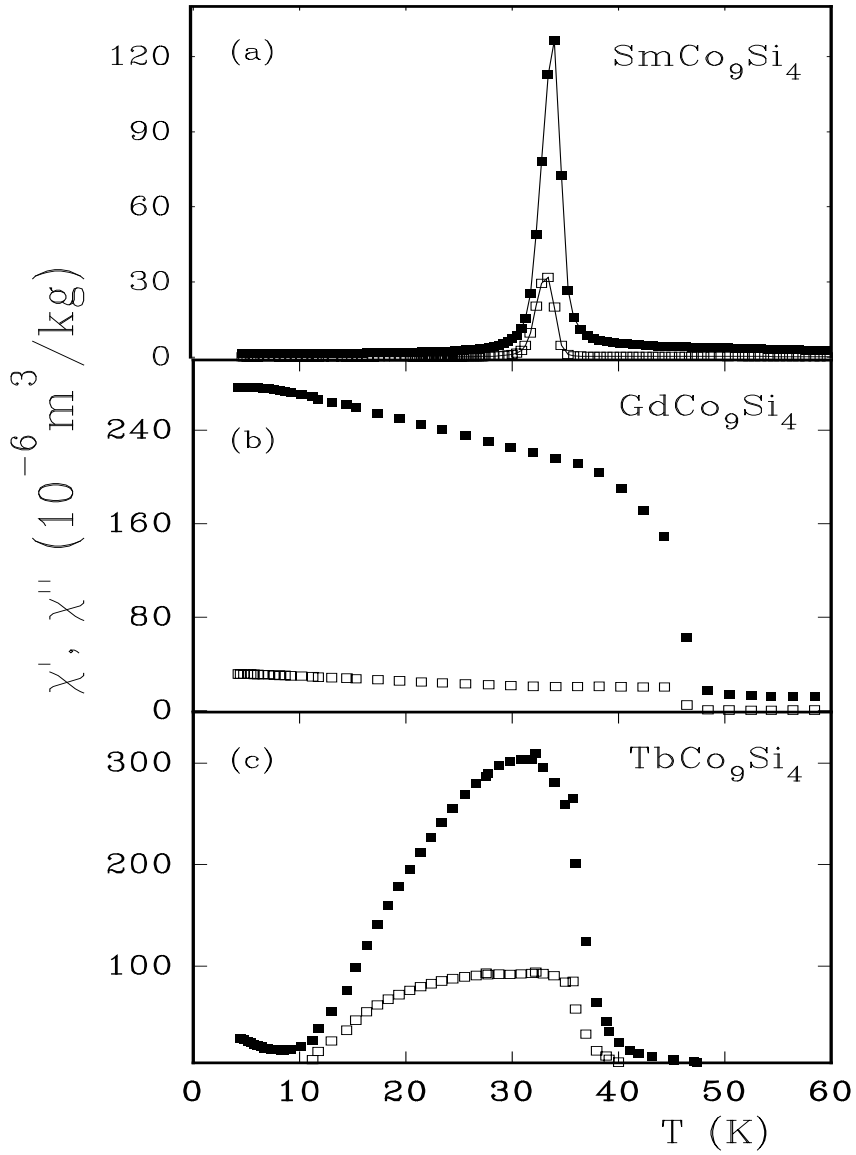

Fig. (2): Temperature dependent ac susceptibility $\chi_{ac}(T)$ of RCo$_9$Si$_4$ compounds with R = Sm, Gd and Tb. Full symbols are the real part (χ') of the ac susceptibility while the open symbols represent the imaginary part (χ'').

Table (1): Structural and transport properties of RCo$_9$Si$_4$

Compound	*a* (Å)	*c* (Å)	T_C (K)	ρ_o ($\mu\Omega$cm)	ρ_{RT} ($\mu\Omega$cm)
SmCo$_9$Si$_4$	7.77700(4)	11.50290(1)	35	23	129
GdCo$_9$Si$_4$	7.76301(4)	11.48652(3)	46	17	108
TbCo$_9$Si$_4$ (A)	7.74961(2)	11.47924(1)	40	10	111
TbCo$_9$Si$_4$ (B)	7.75835(1)	11.48173(2)	20	70	150

Magnetization data versus T, $M(T)$, measured for RCo$_9$Si$_4$ with R = Sm, Gd and Tb in an applied magnetic field of 1T are presented in Fig. (3). The magnetization data thus confirm the occurrence of ferromagnetic transitions in these three compounds. The inset of Fig. (3) shows a broad anomaly in the low temperature magnetization versus temperature data for LaCo$_9$Si$_4$, which cannot be attributed to ferromagnetism rather to spin fluctuations [8], i.e. LaCo$_9$Si$_4$ is a reference system without long range magnetic order.

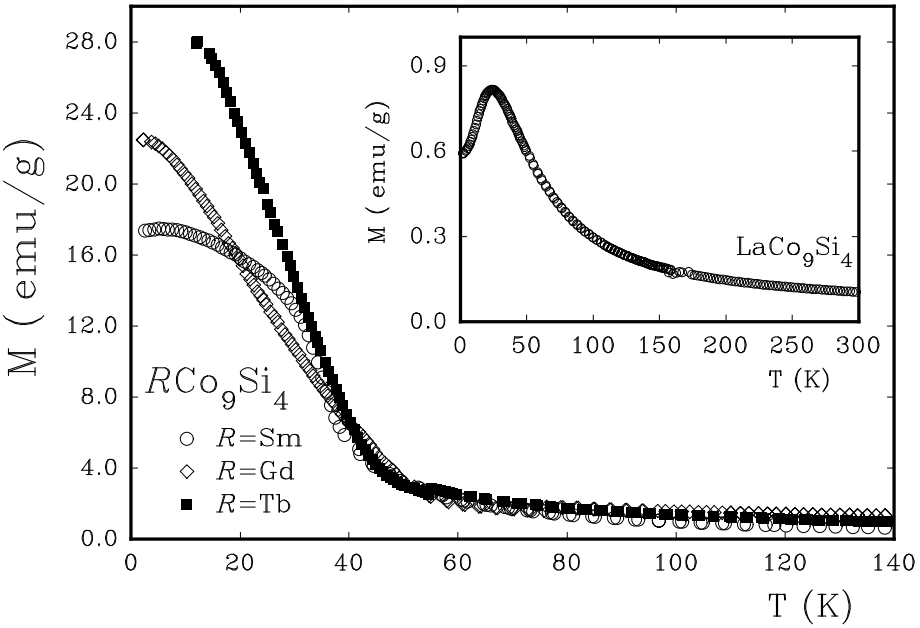

Fig. (3): Magnetization versus temperature $M(T)$ for RCo$_9$Si$_4$ measured in an applied magnetic field of 1T; the inset shows temperature dependent magnetization measured for LaCo$_9$Si$_4$.

As can be seen in Fig. (4) the resistivity data show a kink like anomaly in $\rho(T)$ which are typically for second order magnetic phase transition (see the respective arrows in Fig. 4). Thus, the kink transition indicates a second order

magnetic phase transition in the case of RCo$_9$Si$_4$ with R = Sm, Gd and Tb. However, first order magnetic phase transition has been reported for RCo$_9$Si$_4$ with the lighter rare earth R = Nd and Pr [11]. Similar behaviour has been observed also in the RCo$_2$ compounds and discussed in Refs. [19, 20]. Magnetic ordering temperatures deduced from these anomalies (see the respective arrows in Fig. 4) are in good accordance with those derived from the magnetization, ac susceptibility and specific heat (see below) measurements.

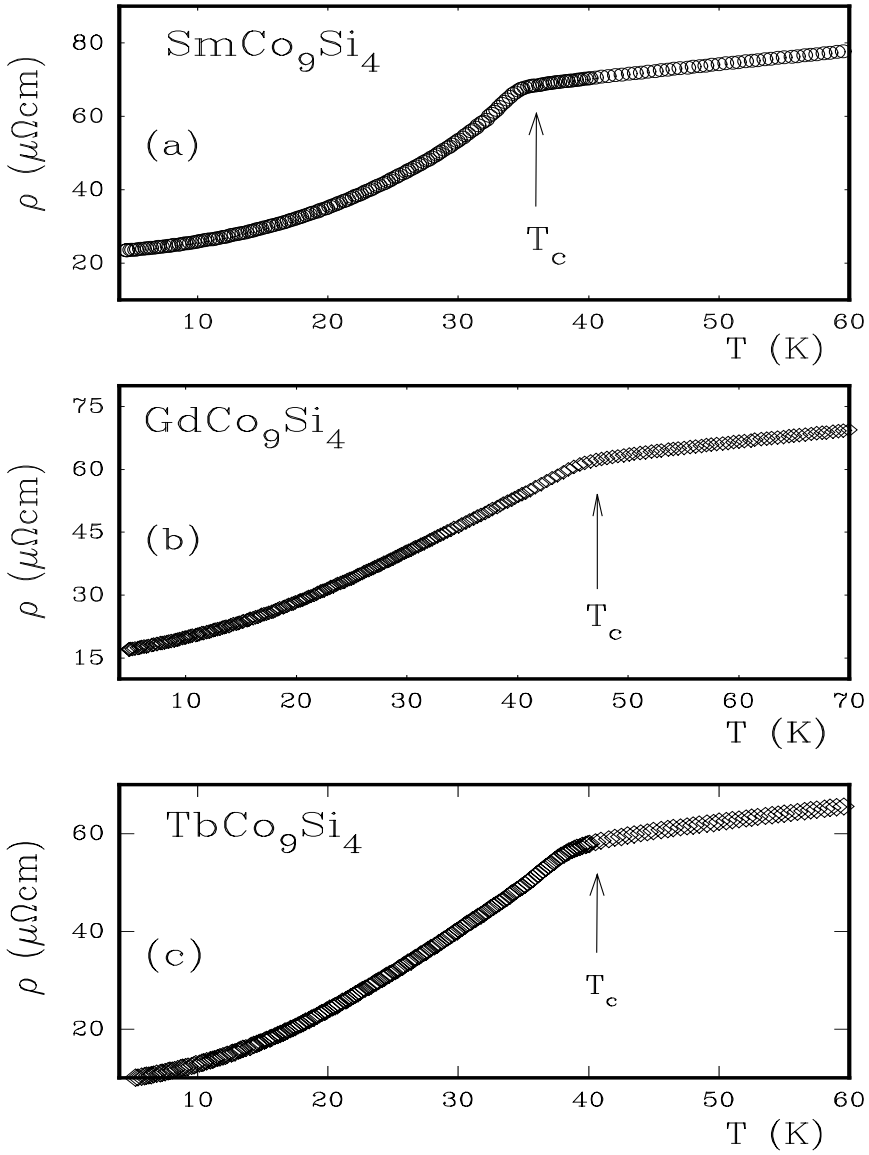

Fig. (4): Temperature dependent electrical resistivities $\rho(T)$ for RCo$_9$Si$_4$ with (a) R = Sm, (b) R = Gd, and (c) R = Tb.

The temperature dependent electrical resistivities of RCo$_9$Si$_4$, with R = Sm, Gd and Tb (see Fig. 4) in the ordered state (below $T_C/2$) are reasonably accounted by the simple relation, $\rho\ (T) = \rho_0 + AT^2$, where ρ_0 is the residual resistivity and A is a coefficient, i.e. there is a quadratic low temperature behaviour as predicted theoretically by Kasuya [21] and Mannari [22] for a ferromagnetic spin wave scenario. The residual resistivities, ρ_0 for the RCo$_9$Si$_4$ (R = Sm, Gd, and Tb) range between 10 and 25 μΩcm (see Table 1). TbCo$_9$Si$_4$ has the smallest residual resistivity values and SmCo$_9$Si$_4$ compound has a relatively large residual resistivity. This indicates that a substantial part of ρ_0 may be due to magnetic fluctuations, because simple potential scattering by lattice defects should result in an approximately constant offset.

The temperature dependent Specific heat $C_p(T)$ for RCo$_9$Si$_4$ (R = Sm, Gd, and Tb) is shown in Fig. (5) as C/T versus T representation. The magnetic phase transitions indicated by the above susceptibility and resistivity data are well resolved in the specific heat data by a jump like anomaly which indicates a second order phase transition for RCo$_9$Si$_4$ compounds, R = Sm, Gd and Tb. It is in good agreement with our conclusions obtained from the resistivity data. This agreement of the susceptibilities, resistivity and heat capacity data is a clear reference to the intrinsic origin of the observed order phenomena. The broad anomalies at low temperature are reminiscent of a Schottky-type anomaly which can be attributed to the level splitting of the rare-earth moments by the molecular field and/or crystal electric field.

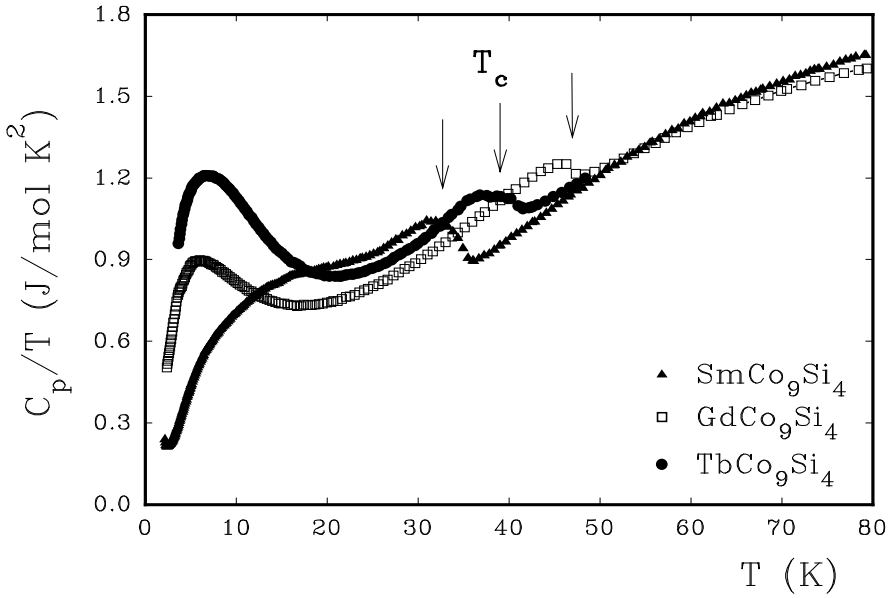

Fig. (5): Temperature dependent specific heat $C_p(T)/T$ versus T for RCo$_9$Si$_4$ with R = Sm, Gd and Tb.

It well known that the magnetic phase transition is related to the exchange interaction. In the rare earth-transition metal intermetallics three types of exchange interactions are responsible for the magnetic phase transition: direct $J_{3d\text{-}3d}$, $J_{R\text{-}3d}$, and indirect $J_{R\text{-}R}$. The latter is much weaker than the $J_{3d\text{-}3d}$. However, there is a competition between $J_{3d\text{-}3d}$ and $J_{R\text{-}3d}$. In the case of $R\text{Co}_9\text{Si}_4$ with R = Sm, Gd, and Tb, the analysis of Curie temperatures, T_c obtained from specific heat data as well as resistivity measurements indicates that the dominant exchange interaction is a direct exchange interaction between Co-Co atoms, $J_{3d\text{-}3d}$. While in our earlier work we reported that the corresponding $R\text{Co}_9\text{Si}_4$ with R in the region of the Pr to Nd exhibit a first order magnetic phase transition which might be attributed to an exchange interaction between rare earth ions and Co, $J_{R\text{-}3d}$, due to larger hybridization and or anisotropy [11].

It is to be noted that there appears to be a rough correlation of the Curie temperature (T_c) reduction with an increase of residual resistivity (indicative for electron scattering on spatial inhogmogeneities of the periodic potential; disorder scattering) for the same stoichiomteric sample prepared with same procedure but treated thermally at different temperatures. We checked the effect of thermal treatment on the stoichiomtery of the samples and prepare two TbCo_9si_4 samples at different annealing temperatures (see above). A direct comparison of the susceptibility, electrical resistivity and specific heat of the TbCo_9Si_4 samples (A and B) is illustrated in Fig. (6).

The existence of an order 1-9-4 phase is corroborated by seven times smaller residual resistivity for sample A as compared to specimen B prepared by the same procedure with different annealing temperature. The Curie temperature of sample B is lower than that value of sample A by about 20 K. This indicate that the five crystallographic positions of the $\text{CeNi}_{8.5}\text{Si}_{4.5}$-type structure are indeed exclusively occupied by individual species of the atoms in the case of stoichiomteric composition (sample A). While sample B reveal a slight reduction in stoichiomteric (off- stoichiomteric composition), result in a random replacement of Co and Si on certain lattice sites.

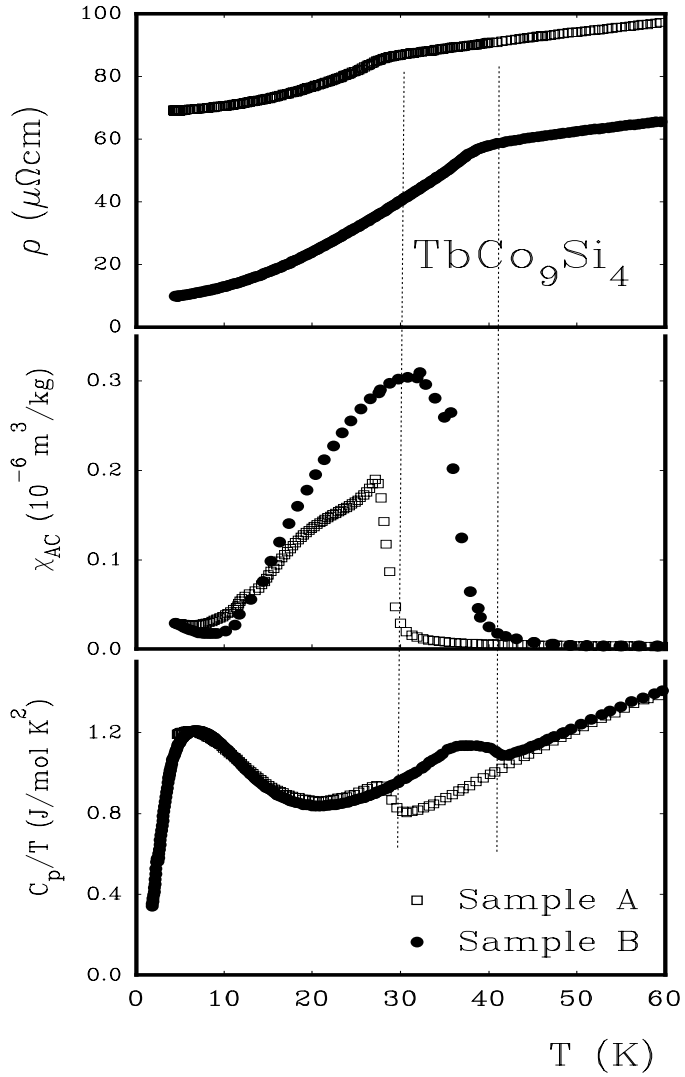

Fig. (6): Temperature dependent resistivity susceptibility, and specific heat measurements of two $TbCo_9Si_4$ samples A and B.

4. Conclusion:

Ternary compounds with fully ordered tetragonal structure RCo_9Si_4 with R = Sm, Gd and Tb have been investigated by means of specific heat, resistivity and magnetization measurements. Ferromagnetic behaviour at low temperature is observed for RCo_9Si_4 (R = Sm, Gd. and Tb) with T_C varying from 30 to 50 K. The temperature dependent electrical resistivities of RCo_9Si_4, in the ordered state (below $T_C/2$) is reasonably accounted by a quadratic power law

behaviour as predicted from ferromagnetic spin wave. The specific heat and transport data indicate a second order magnetic phase transition type for the title compounds which can be attributed to a dominating direct exchange interaction between Co-Co atoms. The straightforward analysis of different stoichiometric samples reveals some correlation between the Curie temperature (T_c) and the residual resistivity (ρ_0).

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References:

1. W. A. J. J. Velge and K. H. J. Buschow, *J. Appl. Phys.*, **39**, 1717 (1968).
2. H. Ido, J. C. Sohn, F. Pourarian, S. F. Cheng and W. E. Wallace, *J. Appl. Phys.* **67**, 4978 (1990).
3. G. H. Rao, J. K. Liang, Y. L. Zhang, X. R. Cheng and W. H. Tang, *Appl. Phys. Lett.* **64,** 1650 (1994).
4. Z. X. Tang, X. H. Deng, G. C. Hadjipanayis, V. Papatfthmiou and D. J. Sellmyer, *IEEE Trans. Magn* **29**, 2839 (1993).
5. M. Q. Huang, Z. Zhang, K. Miller, J. Elbicki, W. E. Wallace, and S. G. Somkar, *IEEE Trans. Magn* **28**, 2859 (1992).
6. M. Q. Huang, W. E. Wallace, R. T. Obermyer, S. Simizu, M. McHenry, and S. G. Sankar, *J. Appl. Phys.* **79** *(8)* 5949 (1996); see also M. Q. Huang, W. E. Wallace, R.T. Obermyer, S. Simizu, and Sankar, *J. Magn. Magn. Mater*. **151,** 150 (1995).
7. R. V. Skolozdra, I. D. Shcherba, O. I. Bodak, G. A. Melnyk, Yu. K. Gorelenko, V. Yarovetz, L. O. Dobryanska, and V. S. Lobojko, *J. Alloys Comp.*,**296,** 272 (2000); see also I. Shcherba, Yu. Gorelenko, Yu. Stadnyk, L Romaka, B. Jatsyk, *Proceedings of 10th Jubilee International Scientific Conference, Achievements in Mechanical & Material Engineering*, **511**, AMME-2001.
8. H. Michor, M. El-Hagary, M. Della Mea. M. W. Pieper, M. Reissner, G. Hilscher, S. Khmelevskyi, P Mohn, G. Schneider, G. Giester and P. Rogl, *Phys. Rev. B* **69**, 081404(R) (2004)
9. H. Michor, M. El-Hagary, S. Öycan. A. Horyn, E. Bauer, G. Hilscher, S. Khmelevskyi, P Mohn, and P. Rogl, *Physics B*, in print

10. M. El-Hagary, H. Michor, E. Bauer, R. Grössinger, P. Kerscl, D. Eckert, K.- H. Müller, P. Rogl. G. Giester, and G. Hilscher, *Physics B,* in print
11. M. El-Hagary, H. Michor, E. Bauer, M. Della Mea, K. Hense, G. Hilscher, *J. Magn. Magn. Mater.* **272**, *e445* (2004).
12. W.Tang, J. Liang, X. Chen, G. Rao, J. Appl. Phys. **76**, 4095 (1994).
13. O. I. Bodak, *Sov. Phys. Crystallogr.* **24,** 732 (1979).
14. W. Tang, J. Liang, Y. Zhao , Y. Guo, G. Rao, and F. Yang, *J. Alloys Comp.*, **226,** 139 (1995).
15. Y. Zhao, J. Liang, G. Rao, Y. Guo, W. Tang, C. Dong, F. Wu,. *J. Alloys Comp.*, **241**, 191 (1995).
16. H. Wei, Z. Lingmin, Z. Yinghong, W. Ziqin, *J. Alloys Comp.*, **298**, 173 (2000)
17. O. Moze. C. H. de Groot, F. R. de Boer, K. H. J. Buschow, *J. Alloys Comp.* **235,** *6*2 (1996)
18. M. El-Hagary, H. Michor, M. Wind, E. Bauer, G. Hilscher and P. Rogl, *J. Alloys Compounds*, **367**, 239 (2004).
19. J. Inoue and M. Shimizu, *J. Phys. F: Metal Phys.*, **12,** 1811 (1982).
20. R. Hauser, E. Bauer, and E. Gratz, *Phys. Rev. B* **57**, 5, 2904 (1998).
21. T. Kasuya, *Prog. Theor. Phys. (Kyoto),* **22,** 227 (1959).
22. Mannari, *Prog. Theor. Phys. (Kyoto),* **22**, 335 (1959).