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Unusual magnetism in $TbRu_2Ge_2$ compound

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ABSTRACT

Magnetic properties of $TbRu_2Ge_2$ were studied. $TbRu_2Ge_2$ shows unusual magnetism, *i.e.* at low field it shows frustration (like spin glass) and at high field, this frustration starts to disappear. It has been found that $TbRu_2Ge_2$ has a T_N of 37K. To confirm the frustration in $TbRu_2Ge_2$, AC susceptibility and normalized magnetization calculations were also performed.

Keywords: Structural; frustration; magnetizations; magnetocaloric.

Introduction

Most of the ternary rare earth intermetallic compound of the type RT_2X_2 [R=Rare earth, T= 3d, 4d, 5d transition metals and X= Si or Ge] crystallizes within the $ThCr_2Si_2$-type body-centred tetragonal structure (*I4/mmm space group*) [**1, 2**]. The R, T and X atoms occupy the 2a, 4d and 4e sites respectively. The atoms are arranged in planes stacked perpendicularly to the c-axis with the sequence of R-X-T-X-R. Rare earth (R)–transition metal (T) intermetallic compounds have interesting magneto-transport and magneto-thermal properties [**3**]. In most of these compounds, magnetic moments are localized only on the rare earth atoms. Many compounds of RT_2X_2 type like $NdRu_2Ge_2$, $GdRu_2Si_2$, $DyRu_2Si_2$, $TbRu_2Si_2$ etc. show uniaxial type magnetocrystalline anisotropy [**5-7**].

Among most of the elements of this series, RRu_2Ge_2 is of great interest because of its unique magnetic properties [**8**]. Another similar and most commonly studied material of RT_2X_2 series RRu_2Si_2. If we take R=Tb, then, there are many similarities between $TbRu_2Ge_2$ and $TbRu_2Si_2$ like both show crystal field effects as reported by Garnier *et al.* [**9-10**]. The other similarity between these two compounds is that they both show multistep metamagnetic behavior at low temperature along [100] direction and both show zero field phase transition below the Neel temperature [**5**]. On the other hand, $TbRu_2Si_2$ has a Neel temperature (T_N) of 53K while that of $TbRu_2Ge_2$ has a value of T_N=32K. Neutron diffraction shows that the magnetic structure of $TbRu_2Ge_2$ is sine modulated below 32K (=T_N) and at 4.2K, it becomes square modulated, with a magnetic moment of 9.06μB [**11**].

Many RT_2X_2 series compounds shows two magnetic transitions, like $NdRu_2Ge_2$ undergoes two successive magnetic transitions at T_t=10K, and T_N=19K [**3**], similarly $NdRh_2Ge_2$ shows two magnetic transitions at 20K and 37K [**12**]. In the present work, we also tried to analyze this phenomenon in $TbRu_2Ge_2$. Garnier *et al.* reported that $TbRu_2Ge_2$ shows complex phase diagrams showing several magnetic structures, depending on field and temperature [**13**]. It has been proved by neutron diffraction measurements that previous studies that [14], a) the huge magnetocrystalline anisotropy of $TbRu_2Ge_2$ favours c axis, b) below transition temperature, $TbRu_2Ge_2$ shows metamagnetic transition.

Experimental

$TbRu_2Ge_2$ polycrystalline samples were synthesized by arc melting. To characterize the annealed samples, powder x-ray diffractograms (XRD), collected using Cu K_α radiation was used. The magnetization (M) measurements were performed both under "zero-field-cooled" (ZFC) and "field-cooled" (FC) conditions, in the temperature (*T*) range of 5 – 150K and up to a maximum field (*H*) of 50 KOe in PPMS (physical property measurement system). Time dependent measurement was also performing in PPMS.

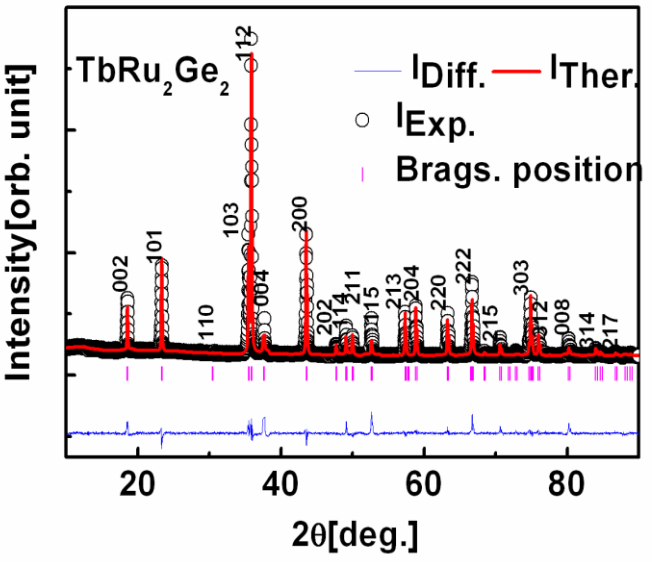

Fig. 1. Rietveld refined powder x-ray diffractograms of $TbRu_2Ge_2$ compound. The plots at the bottom show the difference between the calculated and experimental patterns in each case.

Results and discussion

Fig. 1 shows the room temperature powder X-ray diffraction pattern and Rietveld refinement of $TbRu_2Ge_2$. As can be seen from **Fig. 1**, all peaks can be indexed in $ThCr_2Si_2$ structure in the space group=I4/mmm. The lattice parameters were calculated by refining the XRD data using the Rietveld technique and are a = 4.1142(±3) *Å*, c=10.3043(±1) *Å*, V=174.4311$Å^3$ for $TbRu_2Ge_2$. **Fig. 1** also shows a plot that is the difference between the observed and calculated patterns, the sample is single phase and free from any impurities.

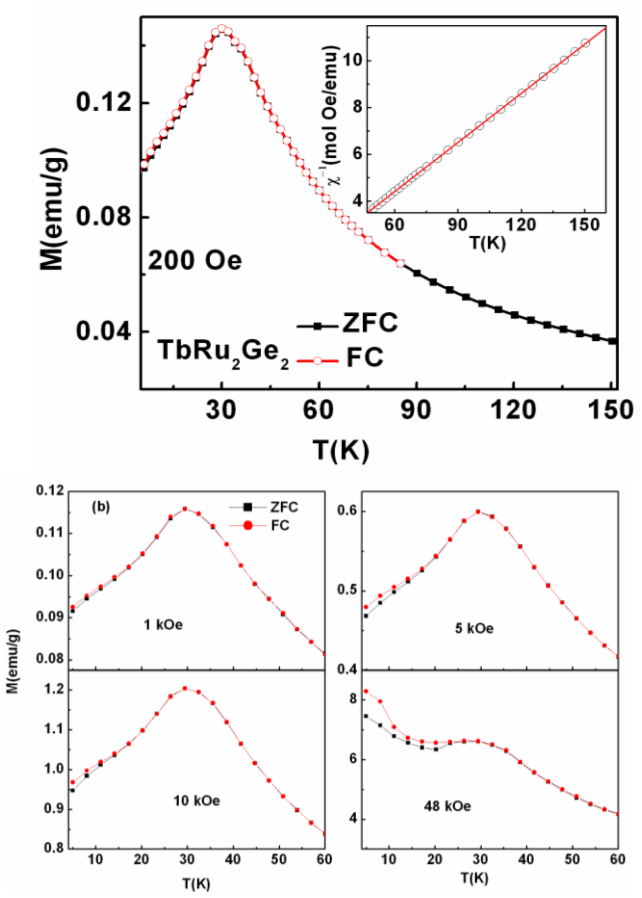

Fig. 2. Temperature dependent of magnetization of $TbRu_2Ge_2$ obtained under (a) 200 Oe and (b) 1, 5, 10 and 48 KOe magnetic field, both under ZFC and FC conditions. Inset shows the temperature dependence of the inverse of susceptibility and Curie-Weiss fit of all compounds.

Fig. 2. shows the temperature dependence of the ZFC and FC magnetization data $TbRu_2Ge_2$. **Fig. 2(a)** shows the data collected in a field of 200 Oe, and it has been found that the difference the ZFC mode and FC curves coalesce in the field of 200 Oe, which is due to frustation. **Fig. 2(a)** tells that at around 37 K, there is a change from paramagnetism (PM) to antiferromagnetism nature (AFM). This is calculated from the d*M*/d*T* vs. T plot. We found that the T_N for $TbRu_2Ge_2$ is 37K, which is in contrast to Yakinthos *et al.* [**11**], who reported the T_N=32K. Inset of **Fig. 2(a)** shows the inverse of susceptibility follows the Curie-Weiss fit $\chi(T) = \chi_0 + C/(T-\theta_{CW})$ in the range 55 K to 155K, which shows that the crystal field effect is an important factor in determining the parameters of $TbTu_2Ge_2$ [**5**]. To further understand the nature of magnetic transition, M-T data was also collected at higher fields, *i.e.*, *H* = 2, 5, 10 and 48 KOe shown in the **Fig. 2(b)**. With an increase in field, the T_N shifts towards a lower temperature, but this shift is very small. A very interesting observation is found from **Fig. 2(b)** that as the applied field is increased from 1 KOe to 48 KOe the ZFC and FC modes start to differ in their paths, and this difference increases with a decrease in temperature. This is due to the fact that at high fields, frustration reduces and magnetic moments start to align.

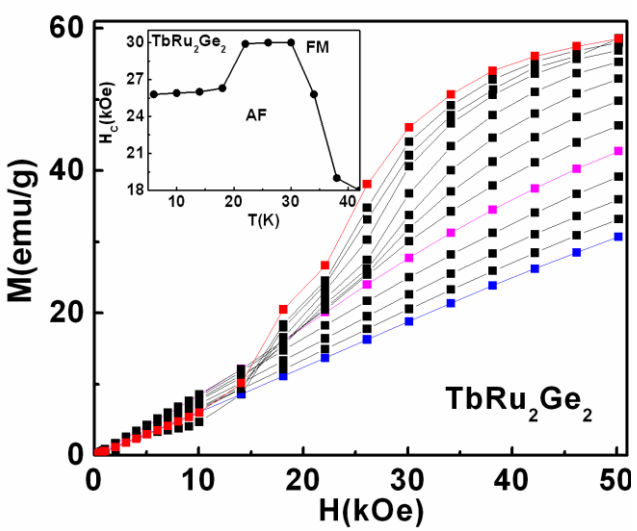

Fig. 3. M-H isotherms near the transition temperature of $TbRu_2Ge_2$ compound. Inset shows the magnetic phase diagram with temperature.

Fig. 3 shows the M-H isotherms, obtained at various temperatures ranging from 5K to 65K in step of 5K close to the ordering temperature, of the $TbRu_2Ge_2$ compound. It can also be seen from the **Fig. 3** that, below a certain field, the high temperature (say 40 K) magnetization value is higher than the low temperature (say 5 K) magnetization value. However, at higher fields, this trend reverses and the low temperature magnetization becomes larger than the high temperature value. This indicates that the compound is antiferromagnetic below a certain field, and above a critical value the application of field takes it to a predominantly ferromagnetic state. Such a field induced transition from an antiferromagnetic state to a predominantly ferromagnetic state has been reported in Tb(Ni,Pd)Al compounds also [**15**]. It is important to note here that, though the M-H isotherms of $TbRu_2Ge_2$ obtained at temperatures above about half of the T_{ord} exhibit metamagnetic transition. Inset of **Fig. 3** shows the temperature variation of the critical field. Initially critical field increases slowly upto 20 K after than jump and in last its decreases with fields.

Fig. 4 shows the AC magnetic susceptibility of $TbRu_2Ge_2$. The AC magnetic susceptibility is magnetic susceptibility which we get by the application of AC magnetic field. AC susceptibility is written as

$$\chi_{ac} = \chi' - i\chi'' \quad (1)$$

In equation (1), χ' and χ'' refers to the real and imaginary component of the AC susceptibility. Real component is also called the in-phase component and imaginary component is also called the out-of phase component. AC susceptibility is used to study the magnetic phase transition [**16**].

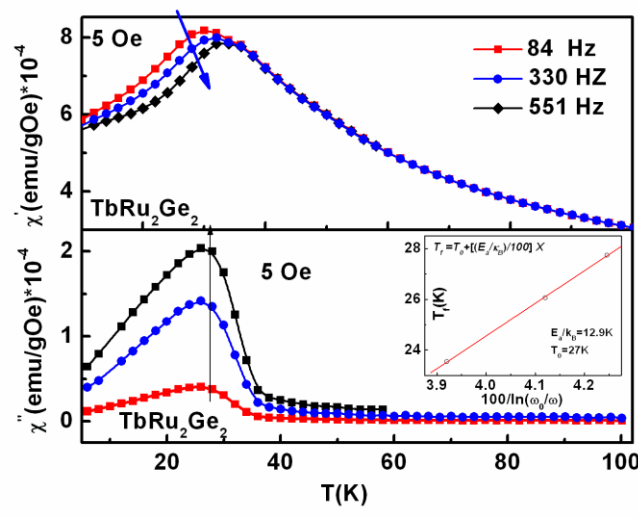

Fig. 4. Temperature variation of the real and imaginary component of the ac magnetic susceptibility of $TbRu_2Ge_2$ in a 5Oe ac magnetic field at various frequencies.

It can be seen that T_f (freezing temperature) of $TbRu_2Ge_2$ is very sensitive with frequency in χ' and χ''. The real AC susceptibility is plotted w.r.t to temperature at different frequencies of 84Hz, 330Hz and 551Hz, in the temperature range of 0 to 100K. The χ' plot shows a peak at T_f ~28K and it shifts towards higher temperature as the frequency changes from 84 Hz to 551 Hz. The out of phase component χ'' also shows a peak at 28K, which rarely shifts to a higher temperature as frequency is changed. Above T_f and at higher temperatures, χ'' is nearly equal to zero, but it has a non-zero value below T_f. This is a characteristic of spin glass transition [17], this is in contrast to disordered AFM systems, where χ'' is constant and remains zero even below transition temperature [**18-20**]. To analyze the frustration (spin glass nature) at low temperature, frequency dependent Vogel-Fulcher law and time dependent magnetization fitting, were also plotted. Inset of figure 4 shows frequency dependent Vogel-Fulcher law, which shows the variation of spin freezing temperature T_f with relaxation time T_0. The AC susceptibility fits well with power law,

$$T_f = T_0 + [(E_a / \kappa_B)/100]X \qquad (2)$$

where, T_0 is 27 K, E_a is activation energy, κ_B is Boltzman constant, and $E_a / \kappa_B = 12.9K$. As can be seen from **Fig. 4** inset, T_f increase linearly with an increase with the logarithmic plot of ω_0/ω, where ω_0 is the attempt frequency ($\omega_0 = \frac{1}{T_0}$) and ω is the operating frequency.

Fig. 5(**a**) shows normalized magnetization M as a function of time in ZFC mode at an applied field of 10KOe. At low temperature, **Fig. 5**(**a**) shows that, the decay of remnant magnetization (or saturation of magnetization) is very slow, which a property of spin glass state. The reason is that in a glassy state, the moments are randomly frozen and to turn those spins along the field direction, field takes a long time [**21**].

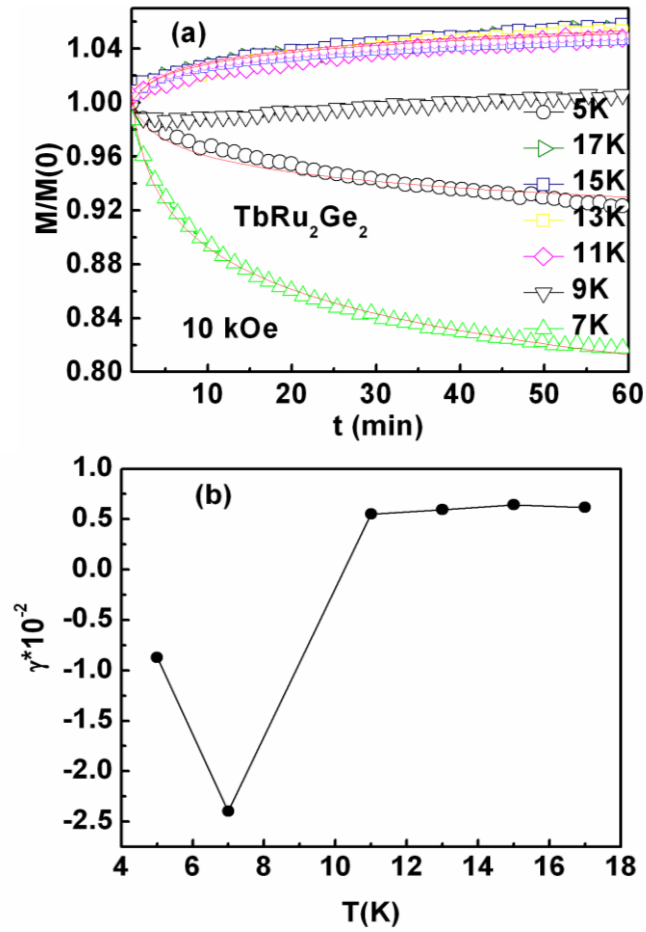

Fig. 5. (a) Normalized magnetization vs time (t) plot for melt spun $TbRu_2Ge_2$ compound measured at different temperature an applied field of 10 kOe in the virgin *H* cycle. For each *H*, *M(0)* is the value of the magnetization recorded when relaxation measurement were started. Solid line shows the calculated curves from equation $M/M(0) = -1 + 2t^{\gamma}$. (b) Temperature dependence of the exponent γ in equation $M/M(0) = -1 + 2t^{\gamma}$ during the constant temperature.

Once we reach to T_f (=7K) and above, we found that the decay of remnant magnetization becomes faster. We can conclude that the application of a field below T_f causes the system to go to an irreversible and metastable state, and above T_f magnetization is independent of time. At low temperature, magnetization follows the law (which is for spin glass):

$$\frac{M}{M(0)} = -1 + 2t^{\gamma} \qquad (2)$$

Fig. 5(**b**) shows the temperature dependence of the absolute value γ which is the exponent of the power law

defined in equation (2). According to Avrami model which is now commonly known as Kolmogorov-Johnson-Mehl-Avrami (KJMA) model for crystallization of solids [**22**], there is an increase in the extent of relaxation during the initial stages of transition due of the formation of newer nuclei, which is dominating. But at higher stages, there is a growth of the product phase, which dominates due to the fact that at higher stages nuclei agglomerate to form bigger cluster [**23**]. **Fig. 5**(**b**) shows that at low temperature γ decreases till 7K, and then it takes a sharp increase. The reason being at low temperature $TbRu_2Ge_2$ shows glassy nature (which is nothing but frustration), and at 7K, there is a formation of an ordered state.

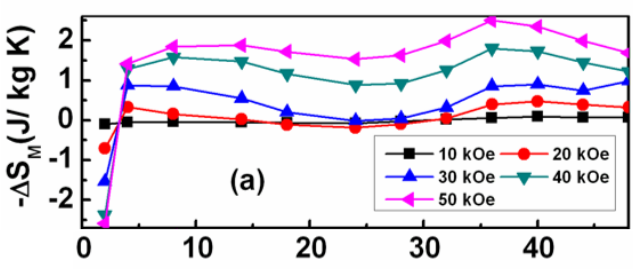

Fig. 6. Temperature variation of isothermal entropy change calculated using the M-H isotherm data.

Fig. 6 shows isothermal entropy change ΔS_M w.r.t temperature, for several values of H (=ΔH) namely 10, 20, 30, 40 and 50 KOe. $TbRu_2Ge_2$ shows very interesting MCE properties. From **Fig. 6**, the entropy change is positive (negative MCE) below ~ 7K (which is due to metamagnetic transition) and it becomes negative (positive MCE) by changing its sign at higher temperatures, giving rise to distinguishable minimum and a maximum for all fields above 10KOe. At around 37K, we get peaks at all the applied magnetic field, which corresponds to the Neel temperature as depicted by **Fig. 2**(**a**). The negative MCE is due to the antiferromagnetic (AFM) nature which has also been proved by neutron diffraction by Shigeoka *et al.* [**24**]. Another interesting phenomenon we observed from **Fig. 6** is that temperature corresponding to maximum entropy change is insensitive to the field. This type of behavior tells us about the ferromagnetism (FM) and antiferromagnetism (AFM) phase coexistence. Shigeoka *et al.* accounted this type of behavior as a mixed magnetic phase due to coexistence of magnetic and non-magnetic.

Conclusion

We have found that $TbRu_2Ge_2$ shows an AFM to FM transition at around 37K (=T_N), and at low temperature it shows a frustration (like spin glass nature). The reason of this frustration is due to the fact that, the moments are randomly frozen and it takes a long time for the field to turn those spins along the field direction. The glassy nature was also confirmed by AC magnetic susceptibility, Vogel-Fulcher law and also by normalized magnetization with time. Specific heat calculations also confirmed that the Neel temperature (T_N) is 37K. Isothermal entropy change ΔS_M w.r.t temperature also confirms the frustration of $TbRu_2Ge_2$ below 7K.

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