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Magnetism, electronic structure and optical properties of $TbNiGe_2$

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ABSTRACT

$TbNiGe_2$ compound crystallizes in the $CeNiSi_2$ type orthorhombic crystal structure and shows antiferromagnetic ordering below 39 K. Magnetization isotherms show linear dependence for field up to 50 kOe. It shows inverse magnetocaloric effect, which is attributed to antiferromagnetic interactions between the moments. The resistivity data was fitted in high and low temperature regimes. The low temperature fit confirms the antiferromagnetic ordering, while the high temperature data follow Bloch-Grüneisen-Mott relation. Ab initio LSDA + U calculations show no spin polarization from Ni 3d electronic states and reproduce the antiferromagnetic long-range ordering of the Tb magnetic moments and their values in good agreement with the previous neutron diffraction data. Optical conductivity data supports the electronic structure calculations and show that it is mostly provided by the transitions involving Ni 3d and Tb 4f electronic states.

1. Introduction

Rare earth intermetallic compounds have received much attention because of their novel magnetic and electrical magnetic properties. These compounds show variety of magnetic phenomena in a wide temperature range from cryo-temperature to above room temperature. Many classes of rare earth intermetallic compounds were studied to search for their potential application such as permanent magnets, magnetocaloric effect (MCE) and magnetoresistance (MR) etc. Some of them such as RT_2 [1], RTX [2], RT_2X_2 [3] and RTX_2 [4] (where R = rare earth, T = transition metal and X = p-block element) are well studied so far. Most of the rare earth intermetallic compounds with the general formula RTX_2 (X = Si, Ge) crystallize in $CeNiSi_2$ type orthorhombic structure [5]. It has been observed that the compounds of $RTGe_2$ series show considerable changes in their magnetic properties when R and T atoms are replaced by other R and T elements [6]. Alsmadi et al. [7] reported that $CeNiGe_2$ undergoes two antiferromagnetic transitions. $NdNiGe_2$ shows ferromagnetic nature at low temperature [8]. Neutron diffraction carried out for $TbNiGe_2$ and $TbNi_{0.4}Ge_2$ shows antiferromagnetic structure with moments oriented parallel to the *c*-axis [9,10]. It has also been observed that only rare earth atom in this series carry magnetic moment. Ivanov et al. [11] performed high field magnetization measurements and found that $TbNiGe_2$ shows a spin-flip transition at 66 kOe field. Salvador et al. [12] reported new compounds such as $RNiGe_2$ (R = Dy–Lu) using molten metal fluxes method. The author reported that these compounds form in new structural arrangements (β) and crystallize in $YIrGe_2$ type orthorhombic structure with space group Immm. It has been observed that electronic structure and magnetocaloric studies are scarcely reported in this series. In addition, there is no report on the optical properties of these materials.

In this paper, we report structural, magnetic, magnetocaloric and transport properties of $TbNiGe_2$. The magnetic properties show low field antiferromagnetic behavior in the compound. Due to antiferromagnetic behavior, MCE in this compound show inverse behavior, which is also manifested by resistivity fitting. The electronic structure calculations and optical properties are also performed to support experimental observations.

2. Experimental and computational details

The polycrystalline sample of $TbNiGe_2$ was prepared by arc melting technique of the constituent elements with purity at least 99.9% in a water-cooled copper hearth. The formed ingot was flipped up and melted several times. As-cast sample was sealed in

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evacuated quartz tube and annealed for 7 days at 800 °C followed by furnace cooling. The X-ray diffraction (XRD) pattern was obtained using X'Pert Pro diffractometer with CuKα radiation (λ = 1.54 Å). Magnetization and transport measurements were performed on physical property measurement system (PPMS-6500). The spectral measurements were performed by the ellipsometric method Beattie at room temperature in the wavelength interval 0.22–15 μm (photon energies E = 0.083–5.64 eV). Mirror-finish sample surface was obtained by means of mechanical polishing with diamond pastes.

To investigate the electronic structure, the LSDA + *U* method was employed [13]. It combines local spin density approximation + *U* correction, as realized in the TB-LMTO-ASA package [14]. A linear muffin-tin (MT) orbitals basis used in this package together with atomic sphere approximation included 6s-, 6p-, 5d- and 4f-states for Tb; 4s-, 4p- and 3d-states for Ni and 4s-, 4p- and 4d-states for Ge. Reciprocal space integration was done using tetrahedra method on a *k*-mesh 8 × 8 × 8. Spin-orbit coupling was not taken into account in these calculations. In the LSDA + *U* method electronic correlations were taken into account for the 4*f*-shell of the rare-earth ions for the following values of direct Coulomb interaction *U* = 5.7 [15] eV and Hund's exchange *J* = 0.7 eV parameters.

3. Results and discussion

The Rietveld refinement of XRD pattern at room temperature shows that $TbNiGe_2$ crystallizes in $CeNiSi_2$ type orthorhombic crystal structure with space group Cmcm. Fig. 1 shows the room temperature XRD pattern with Rietveld refinement. The lattice parameters obtained from the Rietveld analysis are a = 4.09 Å, b = 16.37 Å and c = 4.08 Å.

The susceptibility data obtained in the temperature range of 1.8–300 K in zero field cooled (ZFC) and field cooled (FC) modes in presence of 500 Oe is shown in Fig. 2 (left-hand scale). The cusp in the susceptibility data shows that the compound undergoes an antiferromagnetic ordering below 39 K. The right-hand scale of Fig. 2 shows temperature dependence of inverse magnetic susceptibility along with Curie–Weiss fit, $\chi^{-1} = (T-\theta_p)/C_m$ fit, where θ_p is paramagnetic Curie temperature and C_m is the molar Curie constant. The values of θ_p and paramagnetic effective magnetic moment ($\mu_{eff.}$) estimated from Curie–Weiss fit in the temperature range 80–300 K (T > 2T_N), are found to be −24.7 K and 9.8 μB/Tb^{3+},

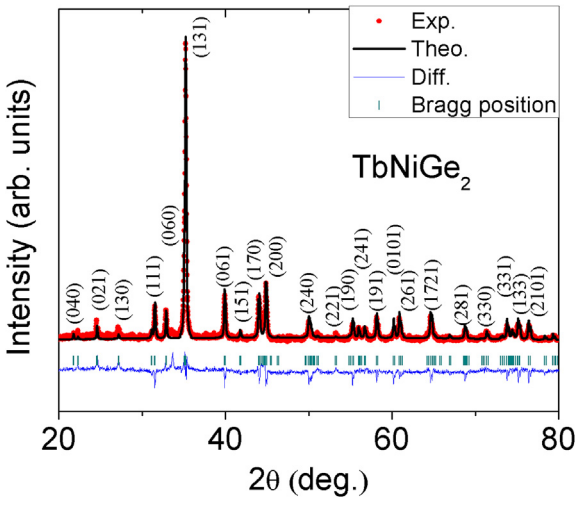

Fig. 1. The room temperature XRD pattern for $TbNiGe_2$.

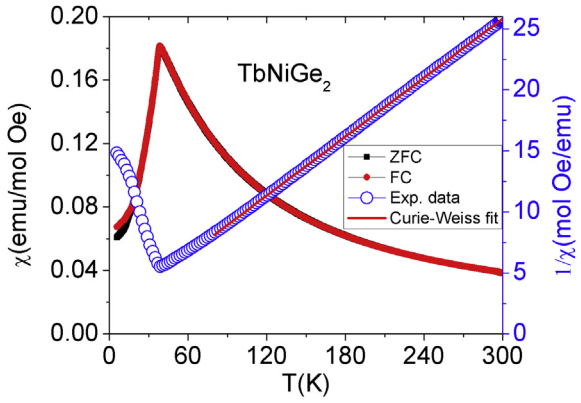

Fig. 2. Temperature dependence of magnetic susceptibility (left-hand scale) and inverse susceptibility along with the Curie–Weiss fit (right-hand scale) in 500 Oe for $TbNiGe_2$.

respectively. The observed value of μ_{eff} is close to the expected g $[J(J+1)]^{1/2}$ value.

The magnetization isotherms were collected in the field up to 50 kOe and are shown in Fig. 3. All the magnetization isotherms show almost linear dependence with field, which confirms antiferromagnetic nature of the compound. As expected, one can note that the magnetization increases with increase in temperature for temperature up to T_N, while above T_N, the magnetization decreases with increase in temperature. The low field magnetization behavior of this compound is in agreement with what reported in Ref. [11].

The magnetocaloric effect manifests as isothermal magnetic entropy change (ΔS_M) is estimated from magnetization data using Maxwell's relation $\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH$ [16]. Fig. 4 shows the temperature dependence of MCE at different fields. It can be noted from Fig. 4 that the compound shows negative MCE (positive ΔS_M) around its ordering temperature. The magnitude of MCE increases with increase in field. At 50 kOe, the compound shows maximum MCE around its T_N. The increase in the magnitude of MCE with field arises due to the change in the orientation of moments on field application. The fact that the MCE is negative even for a field of 50 kOe reflects a strong antiferromagnetic ordering in this compound. Above T_N, the compound shows small positive MCE, which is expected in the paramagnetic regime.

The electrical resistivity has been measured in the temperature range of 2–300 K and is shown in Fig. 5, along with the fit. The resistivity increases with temperature, which reveals the metallic

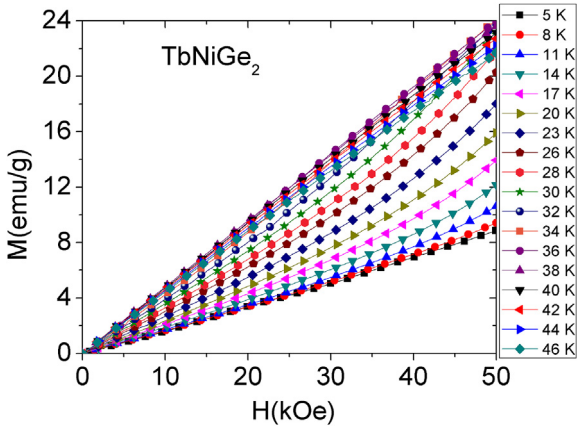

Fig. 3. The field dependence of magnetization at different temperatures in $TbNiGe_2$.