Successive component-separated magnetic transition in TbCoGa₅

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Abstract. We grew single crystals of TbCoGa₅ and measured the magnetic susceptibility, magnetization curves, specific heat and ultrasonic properties. The results of the magnetic susceptibility and specific heat measurements suggest that TbCoGa₅ shows successive component-separated magnetic transition and the degeneracy of quadrupolar degrees of freedom is not fully lifted in intermediate phase. The softening of the elastic constant $C_{44}$ indicates that the degeneracy of electric-quadrupolar (orbital) degrees of freedom exists in spite of the formation of magnetic order. We have considered that the degeneracy of quadrupolar degrees of freedom is important for the occurrence of successive component-separated magnetic transition.

1. Introduction
Some crystallographically uniaxial materials with the spins being geometrically frustrated exhibit unique successive transition characterized by the independent magnetic ordering of the $c$ and $ab$ component of the magnetic moments at the independent temperatures. Here, we call this type of successive transitions "successive component-separated magnetic transition". CsNiCl₃ and DyB₄ are known as two examples of compounds which show such successive transitions.[1]−[3],[4] In the triangular lattice antiferromagnet CsNiCl₃, the higher-temperature ($T_{N1} = 4.84 \text{ K}$) transition corresponds to antiferromagnetic alignment of the Ni spin along the $c$ axis, while the perpendicular part of the moment is paramagnetic. At lower transition temperature ($T_{N2} = 4.40 \text{ K}$), the perpendicular components of the moment becomes ordered. Kadowaki et al. suggested that this type of successive transitions are commonly seen in antiferromagnets having non-collinear spin structure due to competing exchange interaction and weak Ising anisotropies.[3] Recent studies revealed that a Shastry-Sutherland lattice antiferromagnet DyB₄ shows the successive component-separated magnetic transition. The magnetic moments of $c$ and $ab$ components order at independent temperatures, $T_{C1} = 20.3 \text{ K}$ and $T_{C2} = 13.0 \text{ K}$, respectively. Geometrical quadrupolar frustration in addition to geometrical spin frustration play an important role in this system.[4]

In search for another class of successive component-separated magnetic transition, we focused on TbCoGa₅ that crystallizes into the tetragonal HoCoGa₅-type structure ($D_{4h}^2 − P4/mmm$).[5] where TbGa₃ layers and CoGa₂ layers are stacked sequentially along the [001] direction ($c$-axis). Recently Hudis et al. reported that TbCoGa₅ shows two antiferromagnetic transitions at $T_{N1} = 36 \text{ K}$ and $T_{N2} = 5 \text{ K}$ and very weak anisotropy both in its paramagnetic and
ordered state. We grew single crystals of TbCoGa$_5$ and measured the magnetic susceptibility, magnetization curves, specific heat and elastic constants in order to make clear the detail of the successive transitions. The results of magnetic susceptibility and specific heat measurements suggest that two transition temperatures $T_{N1}$ and $T_{N2}$ correspond to those previously reported, however, the magnetic susceptibility is strongly anisotropic. Moreover, we have found that TbCoGa$_5$ shows successive component-separated magnetic transition and the degeneracy of quadrupolar degrees of freedom still exists in intermediate phase between $T_{N1}$ and $T_{N2}$.

2. Experimental

Single crystals of TbCoGa$_5$ were grown by the self flux method. Starting materials were inserted in a quartz tube in the ratio of Tb:Co:Ga=1:1:30 and sealed under high vacuum. This tube was heated up to 750°C and cooled down to room temperature at a rate of $-10\,^\circ$C/hour. Single crystals of TbCoGa$_5$ was identified by means of the X-ray diffraction experiments.

The magnetic susceptibility and magnetization curves of TbCoGa$_5$ were measured using a SQUID magnetometer in the temperature range from 1.8 to 300 K. The specific heat measurement was carried out by the heat-relaxation method down to 2.0 K. The elastic constants of TbCoGa$_5$ was examined by means of ultrasonic measurements. A relative change of the elastic constant $\Delta C$ is obtained by $\Delta C/C = (\Delta v/v)^2$, where $v$ represent the sound velocity. $\Delta v/v$ was measured by a phase comparator using double balanced mixers.

3. Experimental results and discussion

We show in Fig. 1 the temperature dependence of the magnetic susceptibility $\chi$ for the magnetic field $B||[001]$ and $B\perp[001]$. No deference between the field cooling (FC) and zero-field cooling (ZFC) susceptibilities in any direction is observed throughout the whole temperature range; therefore, only ZFC data are shown for clarification. The coincidence of the ZFC and FC data suggests that no spontaneous magnetization is present in TbCoGa$_5$. The susceptibility for $B||[001]$ shows a clear maximum at $T_{N1} \sim 36.2$ K but a small kink at $T_{N2} \sim 5.4$ K. In contrast, those for $B\perp[001]$ shows a small kink at around $T_{N1}$ but a clear maximum at $T_{N2}$. These results allowed us to divided the phase into three temperature regions, which are hereafter called phase I ($T > T_{N1}$), II ($T_{N2} < T < T_{N1}$) and III ($T < T_{N2}$) in the sequence of decreasing temperature.

The magnetic susceptibility above 150 K follows the Curie-Weiss law with the effective paramagnetic moments $\mu_{\text{eff}}$ and the Weiss temperatures $\theta_p$: $\mu_{\text{eff}} = 10.66\,\mu_B$ and $\theta_p = -21$ K for $B||[001]$, and $\mu_{\text{eff}} = 9.84\,\mu_B$ and $\theta_p = -72$ K for $B\perp[001]$. Since the effective paramagnetic

Figure 1. Temperature dependence of the magnetic susceptibilities $\chi$ of TbCoGa$_5$. The inset shows the Curie-Weiss fit (solid lines) to the inverse susceptibility.
moments are close to $9.72\mu_B$ of the free ion value of Tb$^{3+}$, we conclude that the $4f$ electrons in TbCoGa$_5$ are well localized and the Co atoms exist as nonmagnetic ion. The negative values of $\theta_p$ indicate that the predominant magnetic interactions in TbCoGa$_5$ are antiferromagnetic.

The specific heat of the single-crystalline sample of TbCoGa$_5$ shows two $\lambda$-like anomalies at $T_{N1} = 35.5$ K and $T_{N2} = 5.2$ K. Each phase transitions at $T_{N1}$ and $T_{N2}$ is second-order one. The temperature dependence of the magnetic specific heat divided by temperature $C_{\text{mag}}/T$ is shown in Fig.2. The magnetic contribution $C_{\text{mag}}$ to the specific heat of TbCoGa$_5$ is obtained by subtracting the specific heat of isostructural nonmagnetic compound LuCoGa$_5$ from total specific heat of TbCoGa$_5$. We obtain the temperature dependence of the magnetic entropy per Tb$^{3+}$ ion $S_{\text{mag}}$ by numerically integrating the data of $C_{\text{mag}}/T$ vs $T$. The magnetic entropy change reaches $R\ln2$ at $\sim 10$ K and $R\ln6$ at $\sim 36$ K with increasing temperature. Therefore the crystalline electric field ground state of TbCoGa$_5$ is a pseudo-sextet. The temperature dependence of magnetic susceptibilities and specific heat of TbCoGa$_5$ similar to DyB$_4$.[4] In DyB$_4$, the successive phase transition are characterized by a magnetic ordering of $c$ and $ab$ components at independent temperatures, at $T_{C1} = 20.3$ K and $T_{C2} = 13.0$ K, respectively. The magnetic entropy change of DyB$_4$ indicates that the degeneracy of the internal degrees of freedom in intermediate phase is still conserved in spite of formation of magnetic order. Hence, magnetic ordering process of TbCoGa$_5$ should be similar to DyB$_4$.

Figure 3 shows the temperature dependence of the relative change of the elastic constant

![Figure 3](image-url)
\( \Delta C_{44}/C_{44} \) of TbCoGa\(_5\). Here we note that the absolute values of sound velocity could not be measured because of obscure ultrasonic echo signals. The transverse mode \( \Delta C_{44}/C_{44} \) related with elastic strain \( \epsilon_{xy} \) or \( \epsilon_{zx} \) shows a softening of 4.8% from 26 K down to \( T_{N2} \). On the contrary, the longitudinal mode \( \Delta C_{11}/C_{11} \) and the transverse mode \( \Delta C_{66}/C_{66} \) show a smaller softening of 0.2% and 0.7%, respectively. The largest softening of \( \Delta C_{44}/C_{44} \) indicates that the dominant components of the quadrupole moments in TbCoGa\(_5\) are \( O_{yz} = J_y J_z + J_z J_y \) and \( O_{zx} = J_z J_x + J_x J_z \) coupled with the elastic strain \( \epsilon_{xy} \) and \( \epsilon_{zx} \), respectively. Moreover, the elastic softening of \( C_{44} \) are described by the equation \( C_1(T) = C_1^0(T - T_{N1}^0)/(T - \Theta) \) which is deduced from the Curie term of the quadrupole-strain susceptibility. \( \Theta \) is proportional to the average quadrupole-quadrupole interaction between the Tb\(^{3+}\) ions. \( T_{N1}^0 = \Theta + E_{JT} \), where \( E_{JT} \) is Jahn-Teller (4f electron-lattice) coupling. The characteristic temperatures obtained is \( \Theta = 3.9 \) K and \( T_{N2}^0 = 4.0 \) K for \( \Delta C_{44}/C_{44} \). The positive values of \( \Theta \) indicate that the predominant quadrupolar interaction in TbCoGa\(_5\) is ferro-quadrupole. However, we should not conclude whether phase III is ferro-quadrupole state since the absolute value of \( \Theta \) is small. The elastic constant \( C_{44} \) continues to soften above \( T_{N2} \), but exhibits hardening below \( T_{N2} \). These results suggest that the degeneracy of quadrupolar degrees of freedom still exists in phase II, and then the degeneracy of quadrupolar degrees of freedom is fully lifted and the ordered state appears at \( T_{N2} \). Here, we should note that the elastic constants of TbCoGa\(_5\) show no clear anomaly at around \( T_{N1} \). It seems that the quadrupole moments of TbCoGa\(_5\) is not influenced by the magnetic ordering at \( T_{N1} \).

Meanwhile in DyB\(_4\), the elastic constants showed clear anomalies associated with the successive transitions at \( T_{C1} \) and \( T_{C2} \).\(^{[4]}\) The transverse mode \( C_{44} \) exhibits a softening of 40% from \( T_{C1} \) to \( T_{C2} \). The attenuation of the echo signals observed in the intermediate phase suggests that the existence of the fluctuation of quadrupolar moments originating from geometrical quadrupolar frustration. It is considered that the fluctuation of quadrupolar moments plays an important role for the appearance of the successive component-separated magnetic transition in DyB\(_4\).

Considering from the simple tetragonal arrangement of the Tb atoms, it is clear that there is no geometrical frustration in TbCoGa\(_5\). Therefore, spin or quadrupolar frustration is not necessary and at least the presence of the degeneracy of quadrupolar degrees of freedom is important for the occurrence of successive component-separated magnetic transition as the mechanism to suppress the magnetic ordering of the \( ab \) component. Our experimental evidences also suggests that successive component-separated magnetic transition can appear commonly in the rare earth compounds with the degeneracy of quadrupolar degrees of freedom below the highest magnetic transition temperature.

References

[1] N Achiwa 1969 J. Phys. Soc. Jpn. 27 561
[2] R H Clark and W G Moulton 1971 Phys. Rev. B 5 788
[3] H Kadowaki, K Ubukoshi and K Hirakawa 1986 J. Phys. Soc. Jpn. 56 751
[4] R Watanuki, G Sato, K Suzuki, M Ishihara, T Yanagisawa, Y Nemoto and T Goto 2005 J. Phys. Soc. Jpn. 74 2169
[5] Yu N Grin’, Ya P Yarmolyuk and E I Gladyshevskii 1979 Kristallografiya 24 242
[6] J Hudis, R Hu, C L Broholm, V F Mitrovic and C Petrovic 2006 J. Magn. Magn. Mater. 307 301