Magnetic Phase Diagrams with Possible Field-induced Antiferroquadrupolar Order in TbB$_2$C$_2$

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Magnetic phase diagrams of a tetragonal antiferromagnet TbB$_2$C$_2$ were clarified by temperature and field dependence of magnetization. It is noticeable that the Néel temperature in TbB$_2$C$_2$ is anomalously enhanced with magnetic fields, in particular the enhancement reaches 13.5 K for the (110) direction at 10 T. The magnetization processes as well as the phase diagrams are well interpreted assuming that there appear field-induced antiferroquadrupolar ordered phases in TbB$_2$C$_2$.

The phase diagrams of the AFQ compounds in RB$_2$C$_2$ are systematically understood in terms of the competition with AFQ and AFM interactions.

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In addition to spin and charge, an orbital degree of freedom in 3$d$ and 5$d$ electron systems invites an upsurge of interests, because the coupling of the degree of freedom induces novel and rich variety of physical properties. The strong spin-orbit coupling is characteristic to f-electron systems, hence $J$ is the basis of the quantum mechanical description. The magnetic order parameter can be described by a linear combination of $J_{z} \pm$. Depending on the interactions, a higher order term could be the primary order parameter. Quadrupolar ordering may occur without any magnetic contribution. The competitive coexistence of dipolar and quadrupolar interactions and their response to pressure and magnetic field induce novel magnetic phenomena.

Recently Yamauchi et al. reported the antiferroquadrupolar (AFQ) order in the rare earth compound DyB$_2$C$_2$ [1, 2] with the tetragonal LaB$_2$C$_2$-type structure [2, 3]. DyB$_2$C$_2$ undergoes an AFQ transition at $T_Q$=24.7 K. The AFQ order in DyB$_2$C$_2$ was directly confirmed by resonant X-ray scattering technique [1, 2]. Note that $T_Q$ in DyB$_2$C$_2$ is about ten times higher than those of other AFQ materials found to date, though the origin of the strong AFQ interaction is still an open question. Below $T_N$=15.3 K, the antiferromagnetic (AFM) ordering coexists with the AFQ order. The similar coexistent phase has been reported in the isostructural compound HoB$_2$C$_2$ [1, 2]. The AFQ order in the RB$_2$C$_2$ compounds is the first example in which AFQ order is realized in the tetragonal symmetry.

This unusually strong quadrupolar interaction can also be expected in another isostructural compound TbB$_2$C$_2$. TbB$_2$C$_2$ is an antiferromagnet with $T_N$=21.7 K [4]. TbB$_2$C$_2$ shows an anomalous increase of the magnetic susceptibility below $T_N$ [4]. The magnetic structure has quite similar characteristics to phase IV in HoB$_2$C$_2$ which is the AFM phase adjacent to the AFQ ordered phase [10]. Moreover, the magnetization processes that show multi-step field-induced transitions are very similar to those in DyB$_2$C$_2$ and HoB$_2$C$_2$. These unusual properties suggest strong AFQ interactions also in TbB$_2$C$_2$.

A purpose of this study is to clarify the $H$-$T$ phase diagram of TbB$_2$C$_2$ to shed light on this strong AFQ interaction in the RB$_2$C$_2$ system. In this paper, we will report the existence of field-induced AFQ phase and its remarkable stability against magnetic fields. TbB$_2$C$_2$ is the first compound which exhibits the field-induced AFQ ordering. Furthermore, we mention that the phase diagrams in the RB$_2$C$_2$ system are systematically understood in terms of the competing AFQ and AFM interactions.

For sample preparation, we used stoichiometric amounts of the constituents, Tb of 99.9%, B of 99.8% and C of 99.999% in purity. The compound was synthesized through the conventional argon arc melting. Single crystalline sample of TbB$_2$C$_2$ was grown by the Czochralski pulling method using a tri-arc furnace. The magnetization was measured by using a SQUID magnetometer (Quantum Design) and vibrating sample magnetometers with a superconducting magnets of up to 14 T (Oxford Instruments) and a water-cooled Bitter-type steady field magnet up to 15 T installed at High Field Laboratory for Superconducting Materials (HFLSM) of Institute for Materials Research (IMR), Tohoku University. The magnetization processes in higher fields up to 30 T were measured using a pulse magnet and a hybrid-type steady field magnet installed at HFLSM of IMR, Tohoku University.

Figure [1] shows magnetization processes of TbB$_2$C$_2$ measured at various temperatures. The insets show the differential $dM/dH$ curves at 4.2 K as functions of magnetic field. For $H||[100]$, two successive transitions were observed at $H$=7.8 and 8.6 T at 4.2 K. In addition, as clear in the $dM/dH$ curve, a broad anomaly was found around 0.8 T as well. With increasing temperature, the transition at the lowest field becomes broader and shifts to 1.65 T at 22.5 K. This anomaly becomes unclear above 25 K. In contrast, the transitions at 7.8 and 8.6 T shift to lower fields with increasing temperature. These two transition fields approach and merge into a single anomaly at 7.73 T at 14 K. This transition field decreases rapidly and
no anomaly was observed above 25 K.

In case for the (110) field direction, a broad transition around 0.5 T together with a sharp anomaly at 16.9 T was observed at 4.2 K. As temperature increases, the lower transition field increases, whereas the higher transition field decreases and disappears at 28 K. The magnetization process for \( H \parallel [110] \) is identical to that for [110] above 0.4 T, although the [110] axis is inequivalent to [110] in the ground state due to AFM domains. The existence of low field transition is more clearly con-confirmed by our recent neutron diffraction experiments [11].

Figure 2 shows temperature dependence of the magnetization of TbB2C2 under various magnetic fields along the (100) and (110) directions. Curves at higher fields are raised by certain amounts for clarity. Each arrow indicates a critical field defined as a maximum in differential magnetization curves.

This anisotropy is also due to AFM domains[8,9]. However, the increase of magnetization below \( T_N \) was also observed for \( H \parallel [1\bar{1}0] \) above 2 T.

The transition temperature is defined by the temperature of the maximum or minimum of \( d(M/H)/dT \) curves as shown by the arrows in Fig. 2. For \( H \parallel (100) \), we can clearly observe that the transition temperature increases monotonously from 21.7 K to 25.2 K at 5 T with increasing magnetic fields. In general, the AFM transition temperature should be decreased with the application of magnetic fields. At higher fields, the transition temperature suddenly decreases. The fact that no distinct anomaly was observed in the \( M/H \) curve at \( H = 10 \) T indicates that the phase boundary closes between 8 and 10 T.

The unusual behavior that the \( T_N \) increases with the application of fields is further remarkable for \( H \parallel (110) \). The transition at \( T_N = 21.7 \) K shifts drastically to the higher temperature as field increases, and takes the maximum of 35.2 K at 10 T. The transition temperature shows a gradual decrease above 12 T and becomes 31.8 K at 14 T. The close of the phase boundary was not confirmed in this measurement due to the limitation of external field.
The $H$-$T$ magnetic phase diagrams of TbB$_2$C$_2$ for $H_{\parallel}(1\ 0\ 0)$ and $(1\ 1\ 0)$ are shown in Fig. 3. The phase I and IV represent the paramagnetic and AFM states, respectively. Our neutron diffraction study revealed that the magnetic structure in phase IV can be described with the propagation vectors of a dominant $k_2=(0\ 1\ 1/2)$ and an additional $k_4=(0\ 0\ 1/2)$ with a longitudinal sinusoidal modulation $k_L=(1\ \pm\ \delta\ \pm\ \delta,0)$ where $\delta=0.13$. This long periodic modulation $k_L$ is consistent with phase IV of HoB$_2$C$_2$ which is adjacent to the AFQ phase II. The most remarkable feature in the magnetic phase diagram of TbB$_2$C$_2$ is the existence of the field-induced phases (II and III) which are stable in a wide field range from $\sim$0.8 T to 9 T ($H_{\parallel}(1\ 0\ 0)$) and 17 T ($H_{\parallel}(1\ 1\ 0)$). We can clearly recognize that the magnetic field causes the unusual enhancement of the AFM transition temperature as much as 13.5 K for the $(1\ 1\ 0)$ direction in Fig. 3.

In order to identify the phase II and III, the magnetization processes of TbB$_2$C$_2$ were compared with those of DyB$_2$C$_2$ and HoB$_2$C$_2$. Figure 3 shows the magnetization processes of TbB$_2$C$_2$ at 4.2 K together with those of DyB$_2$C$_2$ and HoB$_2$C$_2$ at 1.5 K. The applied magnetic field was normalized with the critical field $H_c$ for $H_{\parallel}(1\ 1\ 0)$ for comparison. As clearly seen, the magnetization curves of TbB$_2$C$_2$ are very similar to those of DyB$_2$C$_2$ and HoB$_2$C$_2$. In the latter compounds, there is a very wide field region where the AFQ phase II is stable, when the field is parallel to the $(1\ 1\ 0)$ direction. (See the lower panel in Fig. 3) Therefore, we tentatively assign that the field-induced phase in TbB$_2$C$_2$ for $H_{\parallel}(1\ 1\ 0)$ would be the AFQ phase. In lower fields, DyB$_2$C$_2$ and HoB$_2$C$_2$ show two-step transitions leading to the phase III and III', in which the AFQ and AFM order coexists.

The difference between phase III and III' is most probably the periodicity along the [001] direction in their magnetic structure. On the other hand, the two-step transition was not clearly observed in TbB$_2$C$_2$. Thus it is indistinct from the present magnetization measurement whether the phase III and III' exist in TbB$_2$C$_2$ for $H_{\parallel}(1\ 1\ 0)$.

When the field is applied along the $(1\ 0\ 0)$ direction, phase III, the coexistent phase of AFQ and AFM order, shows remarkable stability against magnetic fields. The phase III is transformed into the paramagnetic state through the intermediate phase III' in DyB$_2$C$_2$, while the phase III of HoB$_2$C$_2$ directly undergoes magnetic transition to phase I around $H/H_c \sim 0.5$. TbB$_2$C$_2$ also exhibits the successive transitions around $H/H_c \sim 0.5$. Therefore, we suggest that the field-induced phase in TbB$_2$C$_2$ from $H/H_c \sim 0.047$ to 0.46 would be phase III. Furthermore, the successive transition around $H/H_c \sim 0.5$ would be indicative of the existence of the very narrow intermediate phase III'. Neutron diffraction experiments under magnetic fields are highly interesting to confirm the field-induced AFQ phase in TbB$_2$C$_2$. The existence of AFQ ordering in phase II and III stabilized with magnetic field could be interpreted that the strong AFQ interaction does exist in TbB$_2$C$_2$ as well.

The $H$-$T$ phase diagrams in the RB$_2$C$_2$ system can be understood in terms of competition of the AFQ and AFM interactions. The most distinct character in DyB$_2$C$_2$ is the existence of the pure AFQ phase II at $H=0$ without any magnetic contribution. It could be understood that the AFQ interaction is strong enough that the AFQ ordering survives as an intermediate phase to the paramagnetic phase. In case of HoB$_2$C$_2$, however, the pure AFQ...
phase can only be stabilized in finite magnetic fields. For $H=0$, the AFQ ordering is accompanied with the AFM ordering. In TbB$_2$C$_2$, the AFM interaction does not allow AFQ ordering under zero magnetic field, and the AFQ ordering is only realized under magnetic fields. It should be noted, however, that the AFM phase (phase IV) lies adjacent to the AFQ phase and is strongly affected by the AFQ interaction.

The unusual enhancement of $T_N$ with magnetic field is a distinctive character in TbB$_2$C$_2$. The increase of $T_N$ in TbB$_2$C$_2$ reaches 13.5 K which corresponding to $\sim$1 K/T. This enhancement is quite large in comparison with DyB$_2$C$_2$ and HoB$_2$C$_2$. In these compounds, the AFQ transition temperature increases relatively small about 1 K. The increase of $T_Q$ was also reported for other AFQ materials CeB$_6$[14, 15] and PrPb$_3$[16]. In PrPb$_3$ with non-magnetic $I_3$ ground state, the interaction between field-induced octupoles stabilizes the AFQ order. However, the increase of the transition temperature reaches only 0.3 K at 6 T. With respect to CeB$_6$, the AFQ transition temperature $T_Q=3.3$ K is raised to 9.5 K by the external field of 30 T[17]. Recent theoretical works succeeded to explain this anomalous increase of $T_Q$ in CeB$_6$ by taking octupolar interaction into account[18, 19, 20, 21]. An antiferro-type interaction between field-induced octupoles stabilizes the AFQ order against magnetic fields. It is, therefore, supposed that the octupolar moments in TbB$_2$C$_2$ have an important role in the magnetic behavior than that in DyB$_2$C$_2$ and HoB$_2$C$_2$.

In conclusion, the antiferromagnet TbB$_2$C$_2$ is under the strong influence of AFQ interactions. We suggest that TbB$_2$C$_2$ is the first compound which shows the field-induced AFQ ordering. The comparison of the magnetic phase diagrams of TbB$_2$C$_2$ with those of DyB$_2$C$_2$ and HoB$_2$C$_2$ indicates the essential role of competing AFQ and AFM interactions in RB$_2$C$_2$ system.

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