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Magnetic phase diagrams with possible field-induced antiferroquadrupolar order in TbB_2C_2

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Magnetic phase diagrams of a tetragonal antiferromagnet TbB_2C_2 were clarified by temperature and field dependence of magnetization. It is noticeable that the Néel temperature in TbB_2C_2 is anomalously enhanced with magnetic fields, in particular the enhancement reaches 13.5 K for the $\langle 110 \rangle$ 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_2C_2. The phase diagrams of the AFQ compounds in RB_2C_2 are systematically understood in terms of the competition with the AFQ and AFM (antiferromagnetic) interactions.

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In addition to spin and charge, an orbital degree of freedom in $3d$ and f 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 $\boldsymbol{J}$ is the basis of the quantum-mechanical description. The magnetic order parameter can be described by a linear combination of $\boldsymbol{J}_{Z,\pm}$. 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_2C_2[1] with the tetragonal LaB_2C_2-type structure.[2,3] DyB_2C_2 undergoes an AFQ transition at $T_Q = 24.7$ K. The AFQ order in DyB_2C_2 was directly confirmed by resonant x-ray scattering technique.[4,5] Note that T_Q in DyB_2C_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_2C_2.[6,7] The AFQ order in the RB_2C_2 compounds is the first example in which the AFQ order is realized in the tetragonal symmetry.

This unusually strong quadrupolar interaction can also be expected in another isostructural compound TbB_2C_2. TbB_2C_2 is an antiferromagnet with $T_N = 21.7$ K.[8] TbB_2C_2 shows an anomalous increase of the magnetic susceptibility below T_N.[9] The magnetic structure has quite similar characteristics to phase IV in HoB_2C_2 which is the AFM phase adjacent to the AFQ ordered phase.[10] Moreover, the magnetization processes that show multistep field-induced transitions are very similar to those in DyB_2C_2 and HoB_2C_2. These unusual properties suggest strong AFQ interactions also in TbB_2C_2. A purpose of this study is to clarify the H-T phase diagram of TbB_2C_2 to shed light on this strong AFQ interaction in the RB_2C_2 system. In this paper, we will report the existence of the field-induced AFQ phase and its remarkable stability against magnetic fields. TbB_2C_2 is the unique compound which exhibits the field-induced AFQ ordering. Furthermore, we mention that the phase diagrams in the RB_2C_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_2C_2 was grown by the Czochralski pulling method using a triarc furnace. The magnetization was measured by using a superconducting quantums interference device 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_2C_2 measured at various temperatures. The insets show the differential dM/dH curves at 4.2 K as functions of magnetic field. Two successive transitions were observed at $H = 7.8$ and 8.6 T at 4.2 K for $H \parallel \langle 100 \rangle$. A broad anomaly was also found around 0.8 T, as clearly seen in the dM/dH-H curve. 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 $\langle 110 \rangle$ field direction, we observed sharp and broad anomalies around 16.9 T and 0.5 T, respectively, at 4.2 K. With increasing temperature, 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 $[1\bar{1}0]$ above 0.4 T, although the [1 1 0] axis is inequivalent to $[1\bar{1}0]$ in the ground state due to the AFM structures.[8,9] The existence of low-field transition is more clearly confirmed by our recent neutron-diffraction experiments.[11]

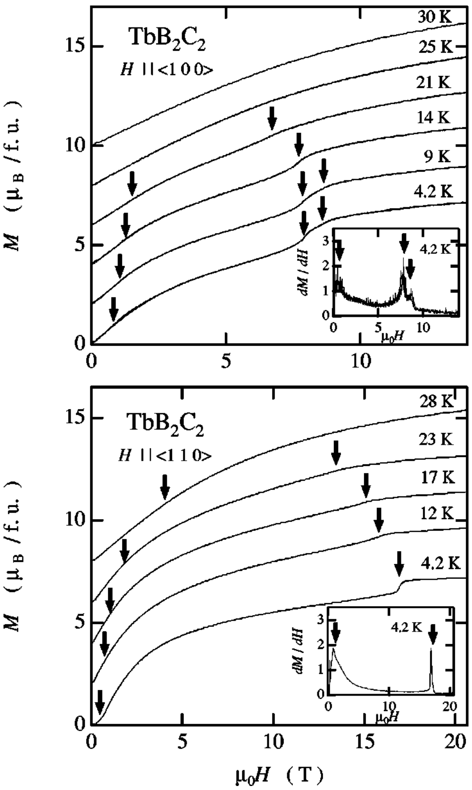

FIG. 1. Magnetization curves at various temperatures of TbB_2C_2 under magnetic fields along the $\langle 100\rangle$ and $\langle 110\rangle$ directions. The inset shows the dM/dH-H curve at 4.2 K for each direction. Curves at higher temperatures are raised by certain amounts for clarity. Each arrow indicates a critical field defined as a maximum in differential magnetization curves.

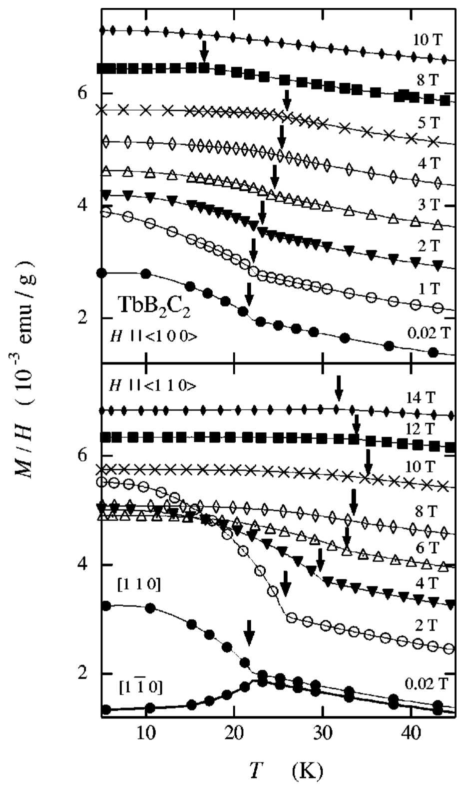

FIG. 2. Temperature dependence of the magnetization of TbB_2C_2 under various fields along the $\langle 100\rangle$ and $\langle 110\rangle$ directions. Curves at higher fields are raised by certain amounts in order to avoid overlapping of the data.

Figure 2 shows temperature dependence of the magnetization M/H at various magnetic fields along the $\langle 100\rangle$ and $\langle 110\rangle$ directions. It should be pointed out that the magnetization increases below T_N though TbB_2C_2 is an antiferromagnet. Usually, the magnetic susceptibility of an antiferromagnet decreases or constant below T_N. This increase of susceptibility was clearly observed for $H<4$ T along the $\langle 100\rangle$. A similar behavior was also found for $H<11$ T along $H\|\langle 110\rangle$. At 14 T for $H\|\langle 110\rangle$, the magnetization turns to decrease with decreasing temperature below T_N. The unusual increase of magnetization is more prominent in $H\|\langle 110\rangle$ than $\langle 100\rangle$. In case for $H\|[1\bar{1}0]$, a cusplike anomaly was observed under 0.02 T. The anisotropic behavior with twofold symmetry is also due to the AFM structures.[8,9] However, the susceptibility for $H\|[1\bar{1}0]$ above 2 T exhibits the same behavior as that for $H\|[1\ 1\ 0]$ originating from the AFM domain switching.

The transition temperature is defined by the temperature of the maximum or minimum of $d(M/H)/dT$-T curves as shown by the arrows in Fig. 2. For $H\|\langle 100\rangle$, 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 usual case, 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-T curve at $H=10$ T indicates that the phase boundary closes between 8 and 10 T for $H\|\langle 100\rangle$.

The unusual behavior that the T_N increases with the application of fields is further remarkable for $H\|\langle 110\rangle$. 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 for $H\|\langle 110\rangle$ was not confirmed in this measurement due to the limitation of external field.

The H-T magnetic phase diagrams of TbB_2C_2 for $H\|\langle 100\rangle$ and $\langle 110\rangle$ are shown in Fig. 3. The phases 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 $\boldsymbol{k}_2=(011/2)$ and an additional $\boldsymbol{k}_4=(001/2)$ with a longitudinal sinusoidal modulation $\boldsymbol{k}_L=(1\pm\delta\pm\delta 0)$ where $\delta=0.13$.[8] This long periodic modulation $\boldsymbol{k}_L$ is consistent with phase IV of HoB_2C_2 which is adjacent to the AFQ phase.[10] The most remarkable feature in the magnetic phase diagram of TbB_2C_2 is the existence of the field-induced phases (II and III) which are stable in a wide field range from ~ 0.8 T to 9 T ($H\|\langle 100\rangle$) and 17 T ($H\|\langle 110\rangle$). We can clearly recognize that the magnetic field cause the unusual enhancement of the AFM transition temperature as much as 13.5 K for the $\langle 110\rangle$ direction in Fig. 3.

In order to identify the phases II and III, the magnetiza-

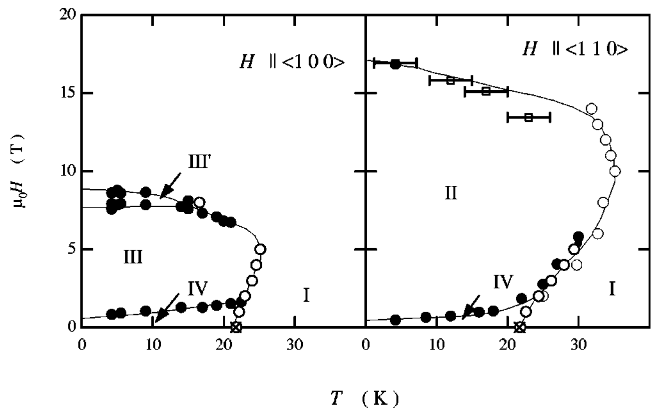

FIG. 3. Magnetic H-T phase diagrams of TbB_2C_2 for the ⟨100⟩ and ⟨110⟩ directions. Closed and open circles indicate phase boundaries determined from the magnetization processes and the temperature dependence of magnetization. Open squares with large errors were obtained from the result of M-H curve using pulse magnet. The Néel temperature determined by specific heat Ref. 8 is shown by the crosses.

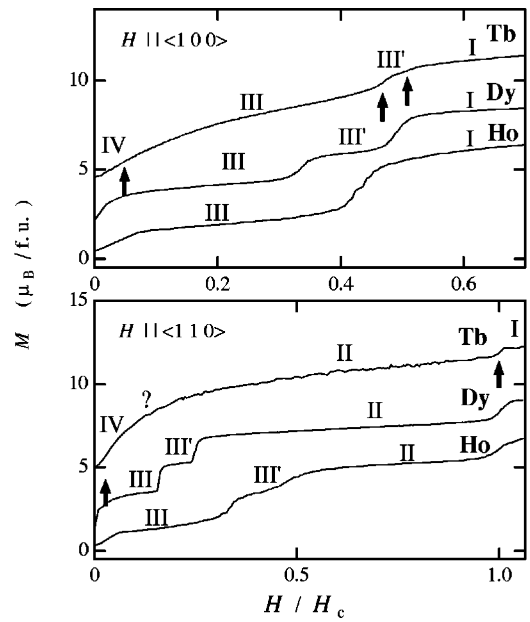

FIG. 4. Magnetization processes of TbB_2C_2 (4.2 K) and DyB_2C_2[1] and HoB_2C_2[6] (1.5 K) for H∥⟨100⟩ and ⟨110⟩. The applied magnetic fields are normalized by the highest transition field in the ⟨110⟩ direction of each compound.

tion processes of TbB_2C_2 were compared with those of DyB_2C_2 and HoB_2C_2. Figure 4 shows the magnetization processes of TbB_2C_2 at 4.2 K together with those of DyB_2C_2[1] and HoB_2C_2[6,12] at 1.5 K. The applied magnetic field was normalized with the critical field H_c for H∥⟨110⟩ for comparison. As clearly seen, the magnetization curves of TbB_2C_2 are very similar to those of DyB_2C_2 and HoB_2C_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 ⟨110⟩ direction. (See the lower panel in Fig. 4.) Therefore, we tentatively assign that the field-induced phase in TbB_2C_2 for H∥⟨110⟩ would be the phase II. In lower fields, DyB_2C_2 and HoB_2C_2 show two-step transitions leading to the phases III and III′, in which the AFQ and AFM order coexists. The difference between phases III and III′ is most probably the periodicity along the [0 0 1] direction in their magnetic structure.[13] On the other hand, the two-step transition was not clearly observed in TbB_2C_2. Thus, it is indistinct from the present magnetization measurement whether the phases III and III′ exist in TbB_2C_2 for H∥⟨110⟩.

When the field is applied along the ⟨100⟩ direction, phase III shows remarkable stability against magnetic fields. The phase III is transformed into the paramagnetic state through the intermediate phase III′ in DyB_2C_2, while the phase III of HoB_2C_2 directly undergoes magnetic transition to phase I around $H/H_c \sim 0.5$. TbB_2C_2 also exhibits the successive transitions around $H/H_c \sim 0.5$. Therefore, we suggest that the field-induced phase in TbB_2C_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_2C_2. The existence of the AFQ ordering in phases II and III stabilized with magnetic field could be interpreted that the strong the AFQ interaction does exist in TbB_2C_2 as well.

The H-T phase diagrams in the RB_2C_2 system can be understood in terms of competition of the AFQ and AFM interactions. The most distinct character in DyB_2C_2 is the existence of the pure AFQ phase without any magnetic contribution. Under magnetic fields, this AFQ phase accompanies induced antiferromagnetic moment. This is called phase II. The AFQ order coexists with the AFM order in the ground state of phase III. The existence of the pure AFQ phase could be understood in terms of strong AFQ interactions in DyB_2C_2. In case of HoB_2C_2, however, the pure AFQ phase cannot be stabilized under zero magnetic fields. Instead, the phase III where the AFQ ordering accompanied with the AFM ordering becomes the ground state. The phase II is only stabilized under magnetic fields. In TbB_2C_2, the AFM interaction does not allow the pure and the coexistent AFQ ordering under zero magnetic field. The AFQ ordering is only realized under magnetic fields as is indicated by phases II and III.

The unusual enhancement of T_N with magnetic field is a distinctive character in TbB_2C_2. The increase of T_N in TbB_2C_2 reaches 13.5 K which corresponds to ~1 K/T. This enhancement is quite large in comparison with DyB_2C_2 and HoB_2C_2. In these compounds, the increase in the AFQ transition temperature is relatively small of 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 nonmagnetic Γ_3 ground state, the interaction between field-induced staggered moments 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.[18–21] 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_2C_2 have an important role in the magnetic behavior than that in DyB_2C_2 and HoB_2C_2.

In conclusion, the antiferromagnet TbB_2C_2 is under the strong influence of AFQ interactions. We suggest that TbB_2C_2 is the unique compound which shows the field-induced AFQ ordering. The comparison of the magnetic phase diagrams of TbB_2C_2 with those of DyB_2C_2 and HoB_2C_2 indicates the essential role of the competing AFQ and AFM interactions in RB_2C_2 system.

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