Evidence of symmetry lowering in antiferromagnetic metal TmB\textsubscript{12} with dynamic charge stripes

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Abstract
Precise angle-resolved magnetoresistance (ARMR) and magnetization measurements have revealed (i) strong charge transport and magnetic anisotropy and (ii) emergence of a huge number of magnetic phases in the ground state of isotopically \textsuperscript{11}B-enriched single crystals of TmB\textsubscript{12} antiferromagnetic (AF) metal with fcc crystal structure and dynamic charge stripes. We analyze for the first time the angular $H-\phi$ phase diagrams of AF state of Tm\textsuperscript{11}B\textsubscript{12} reconstructed from experimental ARMR and magnetization data arguing that the symmetry lowering leads to the appearance of several radial phase boundaries between different phases in the AF state. It is proposed that the suppression of the indirect Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange along $\langle 110 \rangle$ directions between nearest neighboring magnetic moments of Tm\textsuperscript{3+} ions and subsequent redistribution of conduction electrons to quantum fluctuations of the electron density (dynamic stripes) are the main factors responsible for the anisotropy. Essential (more than 25\% at $T = 2$ K) anisotropy of the Neel field in the $(110)$ plane was found in Tm\textsuperscript{11}B\textsubscript{12} unlike to isotropic AF–P boundary in the $H-\phi$ phase diagrams of Ho\textsuperscript{11}B\textsubscript{12}. Magnetoresistance components are discussed in terms of charge carrier scattering on the spin density wave, itinerant ferromagnetic nano-domains and on-site Tm\textsuperscript{3+} spin fluctuations.

Keywords: dynamic charge stripes, lattice instability, electron phase separation, magnetic phase diagram

Supplementary material for this article is available online
(Some figures may appear in colour only in the online journal)
1. Introduction

Rare earth dodecaborides RB₁₂ demonstrate a vast diversity of magnetic and transport properties including ferro- and antiferromagnetic ground states, metal–insulator transition and intermediate valence (see, for review [1–3]) and superconductivity [4, 5]. These compounds have a relatively simple and highly symmetrical UB₁₂-type fcc crystal structure [6], but various simultaneously active interactions in these strongly correlated electron systems make their quantitative theoretical description a difficult task. Indeed, first principles calculations have shown that the B₁₂ molecule stabilizes in distorted states [7] leading to static and dynamic cooperative Jahn–Teller effect shown that the B₁₂ molecule stabilizes in distorted states [7] leading to static and dynamic cooperative Jahn–Teller effect [6]. It was found in [7, 8] that at low temperatures \( T < T^c \sim 60 \text{K} \) in the cage-glass disordered phase [9] the ferrodistortive effect on B₁₂ clusters causes the emergence of spatial modulation of the conduction electron density (dynamic charge stripes), which was confirmed by precise x-ray diffraction experiments on LuB₁₂, provoking also a strong anisotropy of magnetoresistance in combination with Hall effect singularities [10]. So far as the antiferromagnetic (AF) ground state in RB₁₂ with magnetic rare earth (RE) ions is formed by the indirect exchange interaction through conduction electrons (RKKY mechanism), it turns out that this is strongly affected by this (stripe) electron density redistribution. For example, in HoₓLu₁−ₓB₁₂ antiferromagnets it leads to the formation of a complex \( H \rightarrow T \rightarrow \varphi \) magnetic phase diagram with numerous phases [11–13] and with very strong Maltese cross type anisotropy. Taking into account that alike HoB₁₂ also TmB₁₂ shares the same fcc crystal structure with a Jahn–Teller instability of boron sub-lattice and in combination with a very similar multi-q magnetic structure (propagation vector \( q = (1/2 \pm \delta, 1/2 \pm \delta, 1/2 \pm \delta) \) and the same cubic single-ion anisotropy (triplet \( \Gamma_{5/2} \) ground state [14–16]), it is promising to investigate the effect of both the lattice instability and the dynamic charge stripes on the charge transport and magnetic ordering, and to compare these two non-equilibrium antiferromagnets which acquire also a ferromagnetic component with increasing magnetic field above 20 kOe [14, 16].

2. Experimental details

High quality \(^{111}\text{B}\)-enriched Tm\(^{141}\)B₁₂ single crystals were grown using crucible-free inductive floating zone melting in the inert gas atmosphere to prevent boron evaporation. Sample composition was verified by microprobe analysis, and structural quality and crystallographic orientation were checked by x-ray diffraction technique. Detailed information on the preparation of source TmB₁₂ sintered rods as well as details of the crystal growth are presented in [17, 18].

Specific heat (C) and magnetization (M) measurements were carried out on Quantum Design PPMS-9 and MPMS-5XL installations, correspondingly, both in the AF and in paramagnetic (P) states. MPMS SQUID-magnetometer was equipped with rotating sample insert, enabling angular dependencies to be obtained. The stationary sample mount setup provides high precision (∼1%) absolute magnetization values which consider the demagnetizing factor, finite sample size and radial displacement inside magnetometer pickup coils. Charge transport experiments were conducted with an original setup [18], using standard four-points direct current technique with circuit commutation. The axis of sample rotation in this precise angle-resolved resistivity (ρ) measurements was coincided with current direction \( J \parallel ||[110] \) oriented transverse to external magnetic field \( H \perp J \). The studies have been carried out at temperatures in the range 1.8–300 K in magnetic field up to 80 kOe for resistivity, up to 90 kOe for specific heat and up to 50 kOe for magnetization.

3. Experimental results and data analysis

3.1. AF–P transition and charge transport anisotropy in the paramagnetic state

TmB₁₂ is AF metal (see figure 1(a)) with Neel temperature \( T_N = 3.3 \text{ K} \) [19]. The phase transition at \( T_N \) discerns clearly at \( H = 0 \) on the temperature dependencies of resistivity (figure 1(a)), magnetic susceptibility (figure 1(b)) and specific heat (figure 1(c)). The AF state suppressed by external magnetic field is accompanied with emergence of (i) a strong (∼35%) in \( H = 80 \text{kOe} \) negative magnetoresistance (MR) \( \Delta \rho(\rho(H) = \rho(H) - \rho(H = 0))/\rho(H = 0) \) (see figure 1(a)), (ii) a tendency to saturation of magnetization (decrease of low temperature magnetic susceptibility in strong magnetic field, see figure 1(b) and (iii) magnetic Schottky anomaly in the heat capacity at temperatures in the range 2–20 K (figure 1(c)). The low field magnetic susceptibility \( \chi(T) \) demonstrates Curie–Weiss type behavior

\[
\chi = M/H = N_{\text{TM}} \mu_{\text{eff}}^2/(3k_B(T - \theta_p)) + \chi_0.
\]

where \( N_{\text{TM}} = 0.97 \times 10^{22} \text{ cm}^{-3}\) and \( \mu_{\text{eff}} \approx 7.64 \mu_\text{B} \) (\( \mu_\text{B} \) and \( k_B \) are the Bohr magneton and Boltzmann constant, correspondingly) are the concentration of Tm-ions and the effective magnetic moment per unit cell, \( \theta_p \approx -17.2 \text{ K} \) is the paramagnetic Curie temperature corresponding to the AF exchange between these magnetic dipoles and \( \chi_0 \approx 1.03 \times 10^{-7} \mu_\text{B}/\text{Oe} \) is the temperature independent term composed of the diamagnetic susceptibility of the boron cage and Pauli paramagnetism of conduction electrons. A fitting of the experimental curve \( \chi(T) \) by equation (1) indicates that within the limits of experimental accuracy the susceptibility follows the Curie–Weiss dependence with about total Tm\(^{3+}\) magnetic moment in the range 120–300 K. But, as the population of excited magnetic states of the crystal field splitting multiplet \( ^3\text{H}_S \) declines strongly below 120 K [15, 20] the magnetic moment decreases only slightly in the interval 25–120 K (figure 1(d), and a ferromagnetic correlations occur in the range 3.5–25 K. As estimated from equation (1) the changes of effective moment \( \mu_{\text{eff}}(T) \) are shown in figure 1(d). Note, that below 25 K various types of short-range order anomalies were observed previously in TmB₁₂ including a ferromagnetic phase transition detected at \( T_C \approx 2.6 \text{ K} \) [14, 21–23]. Moreover, when temperature decreases into the liquid helium range a double ‘hump-like’ structure of the resistivity curve \( \rho(T) \) can be
component of MR in LuB12 was attributed previously to the field and for deduced from the Curie–Weiss analysis of equation (1).

It is worth noting that sample rotation around the vector even at intermediate temperatures. Depending on $H$ direction the number of anomalies in the AF state changes from one for $|H||[100]$ (marked by $H_{M1}$) in figure 4(a) to three for $|H||[1\bar{T}1]$ and $|H||[1\bar{T}0]$ ($H_{M1}$, $H_{M2}$, $H_{M3}$) in figures 3(b) and (c). At high fields a step-like singularity of susceptibility is observed which corresponds to the location of the Neel field $H_N$ (the AF–P phase transition). As a result, for $|H||[001]$ we observe only one orientation transition at low magnetic field, and the location of AF–P phase detected in TmB12 with natural composition of boron isotopes (81% of $^{11}$B and 19% of $^{10}$B components). Such a dramatic increase of $\rho(T)$ was attributed to magnetic phase transitions at $T_N \approx 3.3$ K and $T_C \approx 2.5$ K in TmB12 [19, 21, 22]. The anisotropy of the magnetic response which is detected in strong magnetic field (figure 1(b), see also figure 4(b)) will be analyzed in more detail in the next sections.

Results of magnetoresistance $\Delta\rho/\rho(H)$ measurements in the external magnetic field up to 80 kOe are shown in figure 2 (see also [24]). Both the field and angular scans at helium temperature $T = 4.2$ K are presented, demonstrating quite different field dependences for various $H$ directions (figure 2(a)) and a rather strong high field MR anisotropy (figure 2(b)) which is similar to that observed in the diamagnetic metallic reference compound LuB12 [7, 8, 10] and in paramagnetic Ho$_x$Luu$_{1-x}$B$_{12}$ solid solutions [11–13, 24]. The anisotropy of the positive component of MR in LuB12 was attributed previously to the charge carriers scattering on dynamic charge stripes along ($1\bar{1}0$) directions. Indeed, it was shown in [7, 8, 10–13, 23, 24] that the interaction of dynamic charge stripes (quantum oscillations of the electron density with a frequency of $\sim 240$ GHz [25]) with strong transverse magnetic field leads to resistivity enhancement for $|H||[001]$ even at intermediate temperatures. It is worth noting that sample rotation around $|H||[1\bar{1}0]$ axis in the transverse configuration allows to vary the $H$ vector in the (110) plane in between three principal crystallographic directions [001], [1$T$1] and [1$T$0] of the cubic structure. Thus, the performed measurements provide the total MR anisotropy in RE dodecaborides. It is seen from figure 2 that in TmB$_{12}$ in paramagnetic state the MR is negative, and in moderate magnetic fields a quadratic isotropic dependence $\sim H^2$ is observed. On the contrary, in strong magnetic field an additional positive anisotropic component appears demonstrating itself with a prominent maximum on MR curves. This result, for $|H||[001]$ we observe only one orientation transition at low magnetic field, and the location of AF–P phase

**Figure 1.** Temperature dependencies of (a) resistivity $\rho$, (b) magnetic susceptibility $\chi$ and (c) specific heat $C$ in magnetic field and for $H = 0$. (d) Effective magnetic moment per Tm ion as deduced from the Curie–Weiss analysis of equation (1).
Figure 2. Field (a) and angular (b) dependencies of magnetoresistance $\Delta \rho/\rho(H, \phi)$ in the paramagnetic phase of Tm$_{11}$B$_{12}$ at $T = 4.2$ K (reproduced from [24]). Dash lines show the correspondence in amplitude between field and angular scans.

Figure 3. Field dependencies of magnetoresistance at different temperatures for $H[\parallel[001]$ (a), $H[\parallel[1\bar{1}1]$ (b) and $H[\parallel[1\bar{1}0]$ (c), and their derivatives $d(\Delta \rho/\rho)/dH(H)$ (d)–(f) correspondingly. Derivative curves are shifted consistently upward to be visible.
boundary located out of the available range of magnetization measurements \((H_N > 50 \text{ kOe, figure 5(a)})\). On the contrary, both for \(H||[1\bar{1}1]\) and \(H||[1\bar{1}0]\) this step-like anomaly is clearly detected on \(\chi(H, T_0)\) curves and can be attributed to the emergence of the field polarized P-state.

Note that for \(H||[1\bar{1}1]\) the \(\chi(H)\) curves demonstrate a very sharp peak preceded by broader maxima and small anomalies can be observed slightly below \(H_N\) (figure 5(c)). Refined \(H–T\) phase diagrams are shown in figure 6 combining the magnetization results with the data obtained from specific heat (see figure S2 in [supplementary information] for more details) and resistivity measurements (figure 3). It is worth noting also that the phase diagram for \(H||[001]\) reconstructed here for \(^{11}\text{B}\) enriched \(\text{Tm}^{11}\text{B}_{12}\) (figure 6(a)) is quite different from that one found previously [21, 22] for \(\text{TmB}_{12}\) with a natural mixture of boron isotopes. Indeed, in [21, 22] three orientation phase transitions have been deduced in the AF-state instead of the only one detected for \(\text{Tm}^{11}\text{B}_{12}\) (figure 6(a)). As a result, one may conclude in favor of an unusual B-isotope effect in \(\text{TmB}_{12}\) which will be studied in future investigations.

It will be shown below that although the phase diagrams in panels (a)–(c) of figure 6 look quite similar, only the low field AF phase (marked as Ia in figure 6) and the high field spin-polarized P-phase are common for all three principal directions of magnetic field. On the contrary, the numerous magnetic phases II–X in figure 6 are peculiarly separated from each other both by radial and circular phase boundaries which characterize distinct regimes of charge carrier scattering and may be attributed to different details of the magnetic structure. The features and regimes of the charge carrier scattering will be in more detail analyzed in the next sections.

3.3. H–\(\varphi\) phase diagrams in the (110) plane at \(T = 2\) K

To specify the location of the phase boundaries for various strength and orientation of \(H\) situated in the (110) plane we have measured at \(T = 2\) K the angular dependences of magnetization \(M(\varphi, H_0)\) and precise angle-resolved \(\Delta \rho / \rho(\varphi, H_0)\) at fixed magnetic fields (see figures 7(a)–(g), correspondingly, and figure 4(b)) from one side, and complementary field dependences of these two characteristics at fixed angles \(\varphi = [001]^\circ H\) in the range 0–90\(^\circ\). Figure 8(a) shows the performed magnetic field derivatives \(dM/dH(H) = \chi(H, \varphi_0)\), the observed MR changes are shown in figures 8(b) and (c). It is seen from figure 8 that the single feature at \(H_{M1}\) observed for \(\varphi = 0\) \((H||[001])\) is transformed into three anomalies at \(H_{M1}, H_{M2}\) and \(H_{M3}\) when \(\varphi\) increases and passes through \(\varphi = 54.7^\circ\) \((H||[1\bar{1}1])\) up to 90\(^\circ\) \((H||[1\bar{1}0])\). Below \(H_N\) another anomalous anomaly is observed [see also MR derivatives in figure S3 in (supplementary information)]. Similar to magnetization (figure 4(a)) the MR in the AF state is about isotropic in the low field interval \(H < 10\) kOe when \(\Delta \rho / \rho\) is positive and has an about linear magnetic field dependence.

On the contrary, above 10 kOe the MR becomes strongly anisotropic and one can distinguish three main angular segments \(\varphi_{01}, \varphi_{110}\) and \(\varphi_{111}\) (see figures 8(b) and (c)), which are located around three principal crystallographic directions and separated one from another by abrupt radial and circular borders. Firstly, the MR anisotropy appears mainly due to the large magnitude anomaly at \(H_{M1}\) and then, either an about linear increase of \(\Delta \rho / \rho(H, \varphi_0)\) (in \(\Delta \rho / \rho(0)\)), or, decrease (in \(\varphi_{111}\)) is observed depending from the sector examined (see figures 8(b) and (c)). It is worth noting that the location of

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**Figure 4.** (a) Field dependencies of magnetization in AF-phase at \(T = 2\) K for \(H\) parallel to three principal crystallographic directions in the fcc lattice, and (b) comparison of enlarged scale angular dependencies of magnetization \(M(\varphi)\) (black curve, left axis) and magnetoresistance \(\Delta \rho / \rho(\varphi)\) (pink curve, right axis) at \(H = 50\) kOe and \(T = 2\) K. Roman numerals denote magnetic phases, P—paramagnetic state.
Figure 5. Magnetic susceptibility $\chi(H, T_0)$ for $H \|[001]$ (a), $H \|[1\bar{1}1]$ (b) and $H \|[1\bar{1}0]$ (c) at different temperatures. Curves are vertically shifted to be better distinguishable.

Figure 6. $H$–$T$ phase diagram of TmB$_{12}$ for three principal directions. Roman numerals denote the magnetic phases.

AF–P transition at $H_N(\phi)$ demonstrates at $T = 2$ K a perceptible anisotropy change from 49 kOe for $H \|[1\bar{1}1]$ to 62 kOe in the orientation $H \|[001]$ (see, for example the dashed line on the right in figure 8(b)). Note also, that when $H$ direction changes inside the $\Delta\phi_{001}$ and $\Delta\phi_{111}$ sectors the phase transition at $H_N$ splits in two, and the lower singularity shifts to lower fields. As these high field anomalies move apart, linear MR range shows in between with negative slope growing in absolute value. We found also some small but discernible MR features in fields $16 \text{kOe} \leq H \leq 26 \text{kOe}$ and $4.5^\circ \leq \phi \leq 20^\circ$, whose location has uncertainty due to hysteresis.

The results of angle-resolved magnetization $M(\phi, H_0)$ and precise angle-resolved magnetoresistance (ARMR) $\Delta\rho(\phi, H_0)$ measurements at fixed magnetic fields shown in figure 7 elaborate the picture of phase transitions in the $(H, \phi)$ plane drawn in field sweep experiments (figure 8). In particular, the $\Delta\rho(\phi, H_0)$ behavior displays a very small anisotropy below 10 kOe, emerging step-like borders between $\Delta\phi_{001}$, $\Delta\phi_{111}$ and $\Delta\phi_{110}$ segments and their transformation when $H$ increases in the range $H_M < H < H_N$. Note, that the anomalies on the angular $M(\phi, H_0)$ and $\Delta\rho(\phi, H_0)$ curves appear at the same directions of $H$ (see, for example, the comparison presented in figure 4(b)) demonstrating synchronous changes in magnetic and charge transport characteristics attributed to orientation phase transitions.

An overall view of the results of $\Delta\rho(\phi, H)$ measurements at $T = 2$ K presented in figures 7(b) and 8(b) and (c) is displayed in figure 9(a) in the cylindrical coordinates where the MR is plotted along the vertical axis and is additionally provided with a color scale. For comparison a similar view of the MR distribution in the paramagnetic state at $T = 4.2$ K is shown in figure 9(c) and the projections of these two data sets onto (110) plane (see figures 9(b) and (d)) allow us to refine the $(H, \phi)$ AF phase diagram ($T = 2$ K, panel (b)) and to link its symmetry with the anisotropy of charge carriers scattering in the P-phase ($T = 4.2$ K, panel (d)). Roman numerals in panel...
(b) show different magnetic I–X phases in the AF state [see figure S5 in (supplementary information) for more details].

It can be seen from figure 9(b) that despite high symmetry of the crystal lattice the magnetic phases for the principal field directions are separated by the radial and circular phase boundaries and, hence, these phases are completely different, and that only one low-field AF state (marked as Ia in figure 6) exists for any magnetic field orientation. The phase boundaries on \( H - \varphi \) diagrams in the (110) plane (symbols in figures 6 and 9(b)) are related to sharp features detected on the \( \Delta \rho / \rho \) angular dependencies, on derivatives of MR and magnetization [figures 8(a) and S3 in (supplementary information)]. Several regions corresponding to phases with different magnetically ordered states and/or regions separated by spin-fluctuation type transitions [26] can be easily resolved in figure 9(b). Similar ‘Maltese cross’ anisotropy in the (110) plane was found recently in related Ho\(_2\)Lu\(_{1-x}\)B\(_{12}\) and Tm\(_{1-x}\)Yb\(_x\)B\(_{12}\) systems [11–13, 27].

4. Discussion

Firstly, we need to mention the similarity of the \( H - T \) and \( H - \varphi \) phase diagrams of TmB\(_{12}\) and HoB\(_{12}\) which are characterized by the same cubic single-ion anisotropy (\( \Gamma_{5(1)} \)) ground state of the \( 4f \) shell and trigonal type (111) easy axis of magnetization) and the alike set of conduction band parameters [28]. Moreover, the same multi-\( q \) incommensurate AF structure characterized by propagation vector \( q = (1/2 \pm \delta, 1/2 \pm \delta, 1/2 \pm \delta) \) with \( \delta = 0.035 \) was detected in [1, 16] both for Ho\(_{11}\)B\(_{12}\) and Tm\(_{11}\)B\(_{12}\) from neutron diffraction experiments at low temperatures in weak (\( H < 20 \) kOe) magnetic fields (\( \delta = 0.038 \) was independently estimated for TmB\(_{12}\) in [15]). For HoB\(_{12}\) it was also shown [14, 29] that as the strength of external magnetic field increases above 20 kOe, the \( 4q \) magnetic structure transforms into a more complex one, in which, apart from the coexistence of two AF \( 4q \) and 2\( q \) components, there additionally arises a ferromagnetic order parameter. Then, a strong modulation of the diffuse neutron-scattering patterns was observed in HoB\(_{12}\) above \( T_N \) [14, 16] with broad peaks at positions of former magnetic reflections, e.g., at (3/2, 3/2, 3/2), pointing to strong correlations between the magnetic moments of Ho\(_{3}^+ \) ions. These diffuse scattering patterns have been explained in [14, 16] by the appearance of correlated 1D spin chains (short chains of Ho\(_{3}^+ \) ion moments placed on space diagonals of the elementary unit), similar to those in low dimensional magnets [30]. It was found that these patterns can be resolved both well above \( T_N \) (up to 70 K) and below Néel temperature, where the 1D chains seem to condense into an ordered antiferromagnetic modulated (AFM) structure [14, 16, 31]. The authors [14] discussed the following scenario for the occurrence of long-range order in HoB\(_{12}\): far above \( T_N \), strong interactions lead to correlations along [111], they are essentially one-dimensional and would not lead to long-range order at finite temperature. As \( T_N \) is approached, the 1D-correlated regions grow in the perpendicular directions, possibly due to other interactions. Cigar-shaped AFM-correlated regions were proposed in [14] that become more spherical when \( T_N \) is approached. Within this picture, the ordering temperature is located in the point where spherical symmetry is reached. Only then 3D behavior sets in, and HoB\(_{12}\) exhibits long-range AFM order [14]. Taking into account the similarities of the magnetic structure, the cooperative Jahn–Teller instability of the boron sub-lattice in these two magnetic dodecaborides and also the same \( \Gamma_{5(1)} \) ground state triplets of Ho\(_{3}^+ \) and Tm\(_{3}^+ \) ions and similar Maltese cross MR anisotropy in HoB\(_{12}\) [13] and TmB\(_{12}\) (figure 9(d)), one can conclude in favor of a common mechanism which is responsible for the suppression of magnetic interaction between the nearest neighbor Tm ions.

As for Ho\(_{11}\)B\(_{12}\), the refinement of Tm\(_{11}\)B\(_{12}\) crystal structure was done with high accuracy in the space group Fm3m, but also small static Jahn–Teller distortions were found in RB\(_{12}\) compounds (reference [6]). However, the most important factor of symmetry breaking is the dynamic one, which includes the formation both of vibrationally coupled R–R dimers and dynamic charge stripes (see references [3, 6] for more details). As a result, the twofold symmetry in the (110) plane is conserved as expected for a cubic crystal, but the charge stripes and Tm–Tm coupled vibrations suppress the RKKY exchange between nearest neighboring Tm-ions, resulting to emergence of complicated phase diagrams with a number of different magnetic phases separated by radial and circular boundaries. In this scenario AF magnetic fluctuations...
well above $T_N$ develop in TmB\textsubscript{12} along trigonal axis [111], and dynamic charge stripes along (110) suppress dramatically the RKKY indirect exchange between Tm magnetic moments provoking the formation of cigar-shaped AFM-correlated regions proposed in [14]. It is worth noting that the fingerprint of symmetry lowering which is the appearance of a number of different magnetic phases with radial and circular phase boundaries between them could not be expected in the case of the only dominating RKKY mechanism of magnetic exchange in these fcc metals with a wide enough (\sim 1.6 eV [32]) conduction band. When comparing the Maltese cross type phase diagrams of HoB\textsubscript{12} [13] and TmB\textsubscript{12} (figure 9(b)), note that in the case of TmB\textsubscript{12} a considerable Neel field anisotropy (more than 25% at $T$ = 2 K) appears additionally with new phases on the $H-\varphi$ diagram in the (110) plane (figure 9(b)). Moreover, phase I is no longer a common for any direction of magnetic field in TmB\textsubscript{12} (see figures 2 and 8(b) and (c)) is also very similar in TmB\textsubscript{12} to that one found previously in the case of HoB\textsubscript{12} [33]. On the other hand, strong and unusual effect in magnetoresistance of TmB\textsubscript{12} is the emergence of negative linear MR term in phase VII detected in the sector $\Delta\varphi_{111}$ (see figure 9(b)). A positive linear MR term deduced in the AF state is traditionally associated with charge carrier scattering on spin and charge density waves (CDWs and CDW\textsubscript{s}) (see, e.g., references [21, 34, 35]). Such behavior is typical, for example, for the itinerant AF phase of chromium, in the absence of Fe and Co magnetic impurities [36] and it has been reported in systems with CDW order including 2H-NbSe\textsubscript{2} [37], Nb\textsubscript{3}Te\textsubscript{2} [38], (PO\textsubscript{2})\textsubscript{4}(WO\textsubscript{3})\textsubscript{8} [39], and RT\textsubscript{2} \textsubscript{3} \textsubscript{3} (\textsubscript{R} = Tb and Ho) [40]. The positive linear MR in the low-field limit has been attributed to a wide range of mechanisms, from magnetic breakdown [37] to scattering on CDW fluctuations at Fermi surface hot spots [40]. Recently the authors [41] have argued that there exists a universal mechanism to create linear positive MR in the low-field/low-temperature limit which is well suited for explaining the behavior of a broad family of density wave materials in which large patches of the Fermi surface are gapped out by the formation of long-range order. The salient features are a consequence of itinerant carriers turning sharp corners of the Fermi surface. This mechanism is greatly enhanced in both CDW and SDW systems, as the formation of correlated electronic states opens a gap at the Fermi surface, removing sheets of open electron paths while keeping only small electron/ hole pockets/ellipsoids with small orbits of sharp curvature. Although only representing a small portion of the Fermi surface, they can manifestly dominate the response to an applied field [41].

On the other hand, the negative quadratic MR component in non-Kondo-type systems with metallic conductivity and localized magnetic moments is attributed usually to electron scattering (i) in a paramagnetic state on a nanometer size clusters of magnetic ions, or (ii) on the on-site $4f-5d$ spin fluctuations in the AF phase [11, 42]. The above mechanisms present in the AF and P states of TmB\textsubscript{12} are accompanied with charge carrier scattering on dynamic charge stripes. Following to [11, 42] we conclude that these fluctuating charges are among the main factors that determine the complexity of the magnetic phase diagram in this strongly correlated electron system. This kind of electronic instability is accompanied with nanometer scale phase separation in combination with local $4f-5d$ fluctuations of electron density in the nearest vicinity of Tm$^{3+}$ ions. The positional disorder in the arrangement of Tm$^{3+}$ ions which are loosely bound in B\textsubscript{24} truncated octahedrons leads in the cagelike state at $T < T^* \sim 60$ K to a significant dispersion of exchange constants (through indirect exchange, RKKY mechanism) and formation of both nanometer size clusters (pairs, triples etc) of vibrationally coupled magnetic Tm$^{3+}$ ions in the RB\textsubscript{12} matrix (short-range order effects well above $T_N$) and to
creation of strong local $4f$–$5d$ spin fluctuations responsible for the polarization of $5d$ conduction band states (the spin-polaron effect). The last one produces spin polarization subnanometer size ferromagnetic domains (ferrons, in the terminology of references [43, 44]) resulting in stabilization of SDW antinodes in the TmB$_{12}$ matrix (see the increase of $\mu_{\text{eff}}$ below 25 K in figure 1(d)). The spin-polarized $5d$ component of the magnetic structure (ferrons) assembled in SDW is from one side very sensitive to the external magnetic field \cite{45, 46}, and, from another side, the applied field suppresses $4f$–$5d$ spin fluctuations by destroying the spin-flip scattering process. Moreover, as it was mentioned above, along the direction of the dynamic charge stripes $[\bar{1}00]$ in the fcc lattice the huge charge carrier scattering destroys the indirect exchange of the nearest neighbored Tm$^{3+}$ localized magnetic moments located at the distance of 5.3 Å from each other, renormalizing the RKKY interaction and accumulating a noticeable part of charge carriers into a filamentary electronic structure. Thus, the complex $H$–$\varphi$ phase diagrams of TmB$_{12}$ antiferromagnet may be explained in terms of the formation of a composite magnetically ordered state of localized $4f$ magnetic moments of Tm$^{3+}$ ions in combination with spin polarized local areas of $5d$ states (ferrons) involved in the formation of SDW in the presence of a filamentary structure of dynamic charge stripes \cite{11, 42}. 

Figure 9. Magnetoresistance $\Delta \rho/\rho = f(H, \varphi)$ of Tm$^{3+}$B$_{12}$ in cylindrical coordinates for current $I||[110]$ at (a) $T = 2$ K (AF phase) and (c) $T = 4.2$ K (P phase) and its projection onto (110) planes (b) and (d) respectively [see (supplementary information) for more details]. Roman numerals in panel (b) show different magnetic phases in the AF state. White points were taken from field scans, yellow ones from angular scans.
Then, turning to the additional negative linear magnetoresistance components appeared solely in phase VII (sector \( \Delta \varphi_{111} \), see figure 9(b)) it is worth noting that this kind of behavior is typical for metallic ferromagnets below Currie temperature, as the magnetic field quenches spin fluctuations and reduces spin scattering of itinerant carriers [47, 48] (see, for example, the magnetoresistance of Ni [49]). From this point of view, in TmB\(_{12}\) the emergence of the negative linear MR term may be attributed to the strong scattering on the spin-polarized (ferron) component of the magnetic structure which is quite different from that one observed in HoB\(_{12}\) [13]. According to estimations of [48] the relation

\[ -\Delta \rho/\rho(H) \sim H/(1 - T/T_C)^{1/2} \]

\((T_C\) is the Curie temperature of ferromagnetic nanodomains) should be valid in this regime, and the linear negative MR term demonstrates an appropriate scaling for TmB\(_{12}\) in \( \Delta \varphi_{111} \) sector below \( T_C \approx 2.5 \text{ K} < T_N \) [see figure S4 in (supplementary information)]. Such features at \( T_C \) were found in this study also on resistivity derivatives \( d\rho/dT(T) \) [figure S4(a) in (supplementary information)] and detected clearly for the Mott thermopower product \( S/T = f(T) \) [see figure S4(c) in (supplementary information), \( S \)—Seebeck coefficient] which was calculated from the data of [50]. Finally, a detailed quantitative analysis of the MR components in three magnetic dodecaborides REB\(_{12}\) (RE—Ho, Er and Tm) is in progress and the results will be published elsewhere.

5. Conclusion

To summarize, the model strongly correlated electron system Tm\(^{11}\)B\(_{12}\) with a fcc lattice instability (cooperative dynamic JT effect) and nanometer size electronic phase separation (dynamic charge stripes) has been studied in detail by low temperature magnetoresistance, heat capacity, and magnetization measurements. The \( H-T \) and angular \( H-\varphi \) magnetic phase diagrams in the form of a Maltese cross with multiple magnetic phases and a notably anisotropic Néel field \( H_N(\varphi) \) have been deduced for the first time in this nonequilibrium AF metal, and matched to three main sectors in vicinity of the main directions (i) \( H||[1\bar{1}0] \) along dynamic charge stripes, (ii) \( H||[001] \) transverse to dynamic charge stripes, and (iii) \( H||[1\bar{1}1] \) connected with the orientation of the AF magnetic structure. A Maltese cross type anisotropy was detected for charge carriers scattering, and three dominated mechanisms of magnetoresistance in the complicated AF state were discussed being attributed to charge carrier scattering on (i) SDW (\( S_d \) component of magnetic structure), (ii) local 4f–5d spin fluctuations of Tm\(^{3+}\) ions and (iii) itinerant ferromagnetic nano-domains composed from spin-polarized conduction electrons. We argue that similar to the case of Ho\(^{11}\)B\(_{12}\) the observed symmetry lowering in Tm\(^{11}\)B\(_{12}\), which leads to the formation of a number of different magnetic phases with radial and circular phase boundaries between them, is a consequence of strong renormalization of the indirect exchange interaction (RKKY mechanism) due to the presence of dynamic charge stripes and the simultaneous emergence of vibrationally coupled Tm–Tm dimers in the matrix of this AF metal. Among distinctions between Ho\(^{11}\)B\(_{12}\) and Tm\(^{11}\)B\(_{12}\) we found the strong Néel field anisotropy (more than 25% at \( T = 2 \text{ K} \)) and the pronounced ferromagnetic linear negative MR component observed in Tm\(^{11}\)B\(_{12}\) for \( H \) directed closely to the trigonal axis.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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