Observation of dynamic charge stripes in $\text{Tm}_{0.19}\text{Yb}_{0.81}\text{B}_{12}$ at the metal–insulator transition

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Abstract
Accurate low temperature charge transport measurements in combination with high-precision x-ray diffraction experiments have allowed detection of the symmetry lowering in the single domain $\text{Tm}_{0.19}\text{Yb}_{0.81}\text{B}_{12}$ crystals that belong to the family of dodecaborides with metal–insulator transition. Based on the fine structure analysis we discover the formation of dynamic charge stripes within the semiconducting matrix of $\text{Tm}_{0.19}\text{Yb}_{0.81}\text{B}_{12}$. The charge dynamics in these conducting nano-size channels is characterized by broad-band optical spectroscopy that allowed estimating the frequency (2.4 × 10$^{11}$ Hz) of quantum motion of the charge carriers. It is suggested that cooperative Jahn–Teller effect in the boron sublattice is a cause of the large-amplitude rattling modes of the Tm and Yb ions responsible for the ‘modulation’ of the conduction band along one of the $\langle 110 \rangle$ directions through the variation of $5d$-$2p$ hybridization of electron states.

Keywords: electronic instability, dynamic charge stripes, nano-size channels

[Supplementary material for this article is available online](#)

(Some figures may appear in colour only in the online journal)

1. Introduction

Dynamic or fluctuating charge and spin stripes attract extraordinary scientific interest due to their possible role in the high temperature superconductivity mechanism [1–14]. While the stripe states were previously thought to be a special feature of the $\text{La}_{2−x}\text{Ba}_x\text{CuO}_4$ family of perovskites [15], phase singularities accompanied by lowered lattice symmetry were detected in a number of other cuprates including $\text{YBa}_2\text{Cu}_3\text{O}_7$ [16, 17], $\text{SmBa}_2\text{Cu}_3\text{O}_x$ [18], $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [19] and $\text{Ca}_{2−x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ [20]. This kind of electronic instability is also suggested to be extremely important for understanding of physics of colossal magnetoresistive manganites [21, 22], nickelates [23–25],
iron-based superconductors [26, 27], heavy fermion hexaborides [28], rare earth dodecaborides [29], etc.

During the last 20 years special attention was paid to find answers to the most significant questions: (1) is there any universal scenario of the dynamic charge and spin stripe formation in the strongly correlated electron systems? (2) How can the dynamic stripes be detected experimentally? Probable origin of conducting stripes is discussed usually from a strong-coupling perspective and various approaches were developed to describe (i) frustrated phase separation (or micro phase separation), (ii) spin–charge ‘topological’ properties, and (iii) valence-bond solid formation [14]. Although the existence of both charge stripes and nematic order in strongly correlated electron systems is now a well-established experimental fact, the origin of these inhomogeneities remains controversial. Taking into account that, from the strong-coupling perspective, stripes are a real-space pattern of microphase separation [8], the nanoscale visualization of the filamentary structure could be realized with the help of scanning tunneling microscopy and scanning tunneling spectroscopy (STM and STS). However, STS and STM are essentially static and surface sensitive techniques and consequently dynamic stripes can only be detected if pinned by impurities. Indirect methods, like anisotropic charge transport measurements on single domain crystals are considered as the most effective technique that enables to detect the symmetry lowering below the transition to fluctuating stripe phase [14]. Among other experiments that recently have been successfully used for observation of dynamic charge stripes, both inelastic neutron scattering [30] and ultrafast and equilibrium mid-infrared spectroscopy [31] should be mentioned. In these studies the lattice fluctuations associated with the dynamic charge stripes were detected in the model compounds—doped nickelates La$_{2-x}$Sr$_x$NiO$_4$ (see also [32]).

Very recently, fluctuating charge stripes have been detected in non-magnetic dodecaboride LuB$_{12}$ [29, 33] and their origin was explained in terms of the cooperative dynamic Jahn–Teller (JT) effect in the boron B$_{12}$ cubooctahedra. More specifically, because of triple orbital degeneracy of the ground electronic state, the B$_{12}$ molecules are JT active and thus their structure is labile due to JT distortions [29]. The presence of intrinsic structural defects (such as boron vacancies and mixed $^{10}$B–$^{11}$B isotope composition of B$_{12}$ molecules) can lift degeneracy due to symmetry lowering and may cause an electronic phase transition associated with JT structural instability. Taking into account that B$_{12}$ clusters form an extended 3D rigid covalent network, being connected by B–B covalent bonds, one can suggest that structural JT liability should retain and reinforce in the boron sublattice of dodecaborides RB$_{12}$ with fcc UB$_{12}$ type structure (see figure 1(a)). The reinforcement due to cooperative dynamic JT effect manifested both in static and dynamic lattice properties should be considered as the cause of large amplitude vibrations (rattling modes) of rare earth ions in oversized B$_{24}$ cages [33] (figures 1(b) and (c)), resulting also in tetragonal distortions of the fcc lattice [29]. The rattling modes of the heavy ions in double-well potentials are shown schematically in figure 1(c), and as a sequence of the quantum motion of $R$-ions the dramatic changes of the 5$d$-$2p$ hybridization of electron states should be expected along the unique crystallographic axis. It results in formation of higher conductive channels—dynamic charge stripes [33] with a strong charge carrier scattering on the nanosize filamentary structure embedded in the RB$_{12}$ fcc matrix. Taking into account that these metallic channels in the rare earth dodecaborides could be better visualized when formed within lower-conducting, dielectric matrix, it looks promising to investigate the stripe signatures in the crystals with chemical composition close to YbB$_{12}$ that is a narrow-gap semiconductor, namely, in the solid solutions of the Tm$_{1-x}$Yb$_x$B$_{12}$ family [34, 35]. That is why for our studies we chose the Tm$_{0.19}$Yb$_{0.81}$B$_{12}$ crystal with isotopically pure boron ($^{11}$B) to avoid any $^{10}$B–$^{11}$B substitutional disorder. Our results of the low temperature resistivity, magneto-resistance and transverse even effect measurements in combination with both precise x-ray diffraction and broadband room-temperature optical studies are presented below. It is shown that dynamic charge stripes in Tm$_{1-x}$Yb$_x$B$_{12}$ may be reliably detected in the difference Fourier maps resulting from the accurate structure analysis. The lower symmetry electron-density distribution is confirmed by the maximal entropy method (MEM) [36]. At low temperatures the filamentary structure is also detected in the measurements of anisotropy of both the magnetoresistance and transverse even effect [35]. Moreover, about an order of magnitude different DC- and far-infrared AC-conductivities are observed at room temperature, which is also indicative of the dynamic stripe formation in the Tm$_{0.19}$Yb$_{0.81}$B$_{12}$ dodecaboride matrix.

2. Experimental details

The details of growth of high-quality Tm$_{1-x}$Yb$_x$B$_{12}$ single crystals, samples preparation and the technique of magneto-transport measurements during sample rotation in a magnetic field are described in [35, 37]. More specifically, the original sample rotation technique applied in the study utilizes a step-by-step freezing (angular step $\Delta \varphi = 1.8^\circ$) of the sample position in the steady magnetic field $\mathbf{H}$, which was perpendicular to the measuring direct current $I$ (for the current $I=1\,\text{mA}$ (see figure 1(d), the vector $\mathbf{n}$ normal to the sample surface $\mathbf{n}||[001]$, angle $\varphi = \psi=45^\circ$). Spherical sample of about 0.3 mm in diameter which is prepared for x-rays data collection is shown in figure 2. In the present study, the same x-ray diffractometers and special software were used to extract fine details of the crystal structure, as it was done recently for LuB$_{12}$ [29, 33]. Broad-band reflectivity measurements of Tm$_{0.19}$Yb$_{0.81}$B$_{12}$ were carried out on a plane, carefully polished sample $\approx 6\,\text{mm}$ in diameter using a set of apparatus, including Vertex 80V Fourier-transform spectrometer, Woollam V- VASE ellipsometer, cw backward-wave oscillator [38] and pulsed TeraView THz spectrometers. Data from [39] were used to extend the reflection coefficient spectra up to $\nu \approx 400\,\text{cm}^{-1}$.
3. Results and discussion

3.1. Magnetotransport anisotropy

Figure 3(a) shows the temperature dependences of the resistivity $\rho(T)$ and the Hall coefficient $R_H(T, H_0)$ of the $\text{Tm}_{0.19}\text{Yb}_{0.81}\text{B}_{12}$ samples. The Arrhenius plot of the data (see figure 1(b) and [35] for details) reveals two activation regimes (regions I and II in figures 1(a) and (b)) on the $R_H(T, H_0)$ curve at $T > 10\, \text{K}$, corresponding to the energy gap $E_g/k_B \approx 200\, \text{K} (\approx 17.8\, \text{meV})$ in this narrow-gap semiconductor (interval I) and the binding energy of the many-body intra-gap states (resonance at $E_F$) $E_p/k_B \approx 75\, \text{K}$ (interval II), respectively. (Here $k_B$ is the Boltzmann constant.) At temperatures below 10 K (figure 3(a), interval III) a transition to a coherent regime of charge transport is observed in the low field region that is suppressed by an external magnetic field of 80 kOe. The low values of the Hall mobility ($3\, \text{–}\, 24\, \text{cm}^2\, \text{V}^{-1}\, \text{s}^{-1}$, see the inset in figure 3(a)) indicate a very strong scattering of charge carriers on charge and spin fluctuations in $\text{Tm}_{0.19}\text{Yb}_{0.81}\text{B}_{12}$. The appropriate scenario of the gap opening in these $\text{Tm}_{1-x}\text{Yb}_x\text{B}_{12}$ conductors was proposed in [35] and the metal–insulator transition was interpreted in terms of formation of Yb–Yb dimers in the matrix of the dodecaborides. In more detail, the formation of randomly disposed ytterbium dimers with the size of $\sim 5\, \text{Å}$ is argued to be the reason of the local (on the scale of the $\text{RB}_{12}$ unit cell ($\sim 7.5\, \text{Å}$) with $E_g \sim 18\, \text{meV}$) gap emerging near the Fermi energy $E_F$ in the conduction band of these compounds. Additionally, the intra-gap many-body states (width of the resonance $E_p \sim 6\, \text{meV}$, see figure 3(b)) developed in $\text{Tm}_{1-x}\text{Yb}_x\text{B}_{12}$ at $E_F$ was explained in [35] as the effect of electronic phase separation with formation of nanosize filamentary structure of conduction channels embedded in $\text{RB}_{12}$ matrix.

Measurements of the charge transport anisotropy at temperature of 2 K in a coherent regime (interval III) are performed in a scheme corresponding to the transverse magnetoresistance and Hall resistance, which are recorded when the crystal rotates around the current axis ($I$) to one of $\langle 110 \rangle \perp \text{H}$, where schematic arrangement of these angular measurements is shown. It is worth noting that in addition to the ordinary Hall effect signal $\rho_H(T, H_0)$ in $\text{Tm}_{0.19}\text{Yb}_{0.81}\text{B}_{12}$ a transverse even effect $\rho_{TE}(\varphi, H_0)$ is also recorded from the Hall probes, and this second harmonic term $\rho_{TE}(\varphi, H_0) = \rho_{HE}\cos 2\varphi$ is directly related to the formation of the filamentary structure of the conducting channels in the semiconducting matrix of the dodecaboride [35]. The procedure of separating the isotropic odd Hall component $\rho_H(\varphi, H_0)$ and the anisotropic transverse
even contribution $\rho_{\text{TE}}$ is described in detail in [35]. Separated families of both resistivity curves $\rho_{\text{anis}}/\rho_0(\varphi, H_0)$ and $\rho_{\text{TE}}(\varphi, H_0)$ are presented in polar coordinates in figures 3(c) and (d), respectively (color shows the amplitude of the resistivity components). It is clearly seen that these two carrier scattering diagrams demonstrate uniaxial anisotropy and the selected axis is located predominantly along the $H || [1 1 0]$ direction for both the resistivity (figure 3(c)) and the transverse even effect (figure 3(d)).

3.2. Crystal anisotropy

It is commonly thought that Tm$_{0.19}$Yb$_{0.81}$B$_{12}$ crystallizes in a cubic lattice. Following this way, we refined its structure in the space group $Fm\bar{3}m$ with the lattice period $a = 7.4679(3)$ Å. However, accurately measured periods of the crystal lattice appeared to be slightly different: $a = 7.4686(5)$, $b = 7.4684(4)$, $c = 7.4668(4)$ Å. Similar ‘tetragonal’ distortion $a \approx b > c$ was observed in LuB$_{12}$ [29]. Difference Fourier synthesis of electron density (ED), which in fact needs no data on crystal symmetry, is used to reveal fine structural details. Calculations were performed using original technique in order to reveal a probable anisotropy of ED. Structure analysis of the dodecaboride is staged. At the first stage, measured values of $|F_{\text{calc}}|$ result from the structure refinement. At the second stage, refined atomic coordinates are distributed over a large volume of the unit cell, all points of which are symmetrically independent in the non-standard $F\bar{1}m$ group chosen to be applied to the input of the Fourier procedure. Updated arrays of $|F_{\text{calc}}|$ were averaged in the cubic $m\bar{3}m$ class since previous $|F_{\text{calc}}|$ were averaged in the cubic $m\bar{3}m$ class and corresponding $|F_{\text{calc}}|$ inherited this feature. Difference Fourier synthesis is performed independently in each point of the new volume to prevent an artificial symmetry overstating as far as possible [3]. Difference Fourier maps (figure 4(a)) show a low-symmetry distribution of difference ED in the faces (1 0 0), (0 1 0), (0 0 1) of the unit cell. The asymmetry of ED distribution is confirmed by processing the structural data using the maximal entropy method.
MEM [36], which does not need atomic coordinates and chemical composition to restore ED from observed structure factors $F_{\text{obs}}$. For comparison, MEM maps in the three faces are presented in figure 4(b). MEM reconstructs total but not difference ED, so that light boron atoms are as clearly seen as heavy $R$ atoms. As is clear from figure 4, the traces of conducting channels are observed along the face diagonals $[0 1 1]$, $[1 0 \overline{1}]$, $[1 1 0]$, but the most pronounced charge stripes are detected along $[1 0 \overline{1}]$ in the $(0 1 0)$ plane.

3.3. Dynamic conductivity

The broad-band reflectivity spectrum of the Tm$_{0.19}$Yb$_{0.81}$B$_{12}$ single crystal is presented in figure 5(a). With the Kramers–Kronig analysis, the spectrum of dynamical conductivity was calculated, as shown in figure 5(b). Rich set of peaks in the spectrum was modeled with the sum of Lorentzian expressions

$$\sigma^*(\nu) = \sigma_0 \frac{0.5 \Delta \varepsilon_0}{\nu \gamma + i(\nu^2 - \nu_0^2)}$$

where $\Delta \varepsilon_0$ is the dielectric contribution, $\nu_0$ is the resonance frequency and $\gamma$ is the damping constant. The details of the conductivity spectrum analysis and parameters of corresponding excitations will be published elsewhere (see also supplementary table 1). Among the most important results, two issues should be mentioned here: (i) the value of conductivity at terahertz frequencies, $\sigma(30–40 \text{ cm}^{-1}) \approx 1500 \, \Omega^{-1} \, \text{cm}^{-1}$, is about an order of magnitude below the measured DC conductivity $\sigma_{\text{DC}} \approx 13\,000 \, \Omega^{-1} \, \text{cm}^{-1}$ and (ii) modeling the mismatch with the Drude conductivity term (dashed line in figure 5(b)) $\sigma(\nu) = \sigma_{\text{DC}} (1 - \nu^2 / \nu_0^2)^{-1}$ provides the scattering rate of carriers $\gamma \approx 8 \, \text{cm}^{-1}$, which coincides very well with the damping of two quasilocal vibrations of the heavy $R$-ions (Tm and Yb) located at 107 cm$^{-1}$ (~154 K) and 132 cm$^{-1}$ (~190 K) (see supplementary table 1). For comparison, similar values of Einstein temperature $\Theta_E = 160–206$ K have been detected previously in EXAFS [40], heat capacity [41] and inelastic neutron scattering [42] studies of the dodecaborides. Taking into account that these rattling modes induce variation of $5d$-$2p$ hybridization in $RB_{12}$ [29], we suggest that this kind of ‘modulation’ of the conduction band is responsible for the dynamic charge stripes formation in the dodecaboride matrix. Besides, the frequency $\sim 2.4 \times 10^{11}$ Hz ($8 \, \text{cm}^{-1}$) can be deduced from the conductivity spectra as the characteristic of the quantum motion of charges in the dynamic stripes. As a result, the room-temperature DC conductivity in Tm$_{0.19}$Yb$_{0.81}$B$_{12}$ should be attributed to the charge transport in dynamic stripes that are more conductive than surrounding semiconducting matrix. Consequently, the value of the DC conductivity is determined by the stripes that percolate through the crystal while relatively smaller AC conductivity is provided by the THz-FIR reflectivity of the ‘whole’ sample (conducting stripes + semiconducting matrix).

4. Conclusion

A set of experimental results is obtained that evidence formation of dynamic charge stripes within the semiconducting matrix of Tm$_{0.19}$Yb$_{0.81}$B$_{12}$. The uniaxial anisotropy of the magnetoresistance and transverse even effect is observed in the single domain face-centered cubic Tm$_{0.19}$Yb$_{0.81}$B$_{12}$ crystals. Accurate x-ray diffraction experiment and structural data analysis combined with the reconstruction of difference Fourier maps of the
residual electron density and applying the maximum entropy method to deduce the normal electron density allowed to visualize the dynamic charge stripes and symmetry lowering. Taking into account that many strongly correlated electron systems including CMR manganites and HTSC are inhomogeneous at part of structure analysis.

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