Superconductivity, Magnetoresistance, Magnetic Anomaly and Crystal Structure of New Phases of Topological Insulators Bi$_2$Se$_3$ and Sb$_2$Te$_3$

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Abstract. We synthesized a new metastable phase of Bi$_2$Se$_3$ topological insulator by a rapid quenching after a high-pressure-high-temperature treatment at $P \approx 7.7$ GPa, $673<T<1400$ K. The structure of metastable phase is monoclinic $P2_1/m$ type. We observed the zero-field magnetic susceptibility cusp and linear positive magnetoresistance indicating the topological insulator state. The annealing at 673 K during 2 hours resulted in complete reversible transformation into the initial crystalline rhombohedral structure. Also we synthesized bulk polycrystalline samples of metastable at ambient conditions monoclinic (C2/m) phase of Sb$_2$Te$_3$ by rapid quenching after a high-pressure–high-temperature treatment at $P=3.7–7.7$ GPa, $T=873$ K and found superconductivity with $T_c=2$ K. A zero-field magnetic susceptibility cusp and linear positive magnetoresistance indicate a topological insulator state.

1. Introduction

Experimental studies of bismuth and antimony chalcogenides substantially intensified last years due to discovery of their topological insulator (TI) properties [1-13] predicted earlier theoretically. Among other unusual properties of these materials superconductivity attracts much attention as far as it may possess the unconventional p-wave type. The unconventional superconductivity features have been indeed observed in Cu doped Bi$_2$Se$_3$ [7,8] and specially sintered Sb$_2$Te$_3$ [13]. Mostly the superconductivity in TIs was observed "in situ" under high-pressure [8,9]. In particular, in Bi$_2$Se$_3$ superconductivity appeared under pressure of 11 GPa with the critical temperature rising from 0.5 to 7 K under pressure up to 30 GPa, and the upper critical magnetic field of transition increased from 0.3 up to 4 T in the pressure range of 13-30 GPa [8]. The reduced critical field $h^*(T)=(H_{c2}(T)/T_c)/(dH_{c2}(T)/dT)|_{T_c}$ was calculated and compared to the models for orbitally limited s-wave and spin-triplet p-wave superconductors and found that the experimentally defined value of...
about h*(0) = 0.9 exceeded the upper limits of 0.7 for s-wave and 0.8 for the spin-triplet p-wave case. Thus the p-wave superconductivity type was concluded.

By applying high-pressure the superconducting phases have been also found in other TIs like tellurides of Bi [9], Sb [10], In [12] and selenides Sb$_2$Se$_3$ [11]. However, the transitions to superconducting phases were reversible as well as in Bi$_3$S$_3$. After the pressure releases they transformed back to non-superconducting phases. Besides superconductivity the peculiar properties of TIs like linear positive magnetoresistance effect and the zero-field paramagnetic cusp were observed [13,14].

Here we present synthesis of new Bi$_2$Se$_3$ metastable phases with monoclinic crystal structures by quenching after high-pressure-high-temperature treatment at high pressure and different temperatures and metastable superconducting phase Sb$_2$Te$_3$, linear positive magnetoresistance effect at low temperatures and the zero-field paramagnetic cusp at T=100 K and 300 K indicating topological insulator state.

2. Experimental

We used the commercially available high-purity (99.999%) Bi$_2$Se$_3$ and Sb$_2$Te$_3$ alloys with rhombohedral structure [15]. We have synthesized metastable high-pressure phases by rapid quenching after the electrical current thermo resistive heating in the "anvil with cavity"-type high-pressure apparatus [14]. The high-pressure-high-temperature experiments were carried out up to 7.7 GPa pressure with the heating up to 1673 K. The sample cooling rate was ≈ 60°/min, and its pressure reduction rate in the reaction cell ≈ 1 GPa/min. The output samples were 2.5 mm thick and 4.5 mm in diameter. Metastable phases m-Sb$_2$Te$_3$ has monoclinic C2/m structure [16].

For the analysis of the crystal structure and physical properties of the samples we employed the powder X-ray diffraction, electrical, magnetic, and heat capacity measurements. PANalytical diffractometer with CuKα radiation source was used. We studied the temperature dependencies of the electrical resistivity of the samples via a conventional 4-probe method down to 1.8 K, current-voltage characteristics, effect of magnetic field up to 9 T and the heat capacity by differential scanning calorimetry in the temperature range of 1.8 - 400 K using the Quantum Design® physical properties measurement system (PPMS) 3.

3. Experimental results

3.1. Crystal structure of metastable phase of m-Bi$_2$Se$_3$.

Fig. 1 shows the change in the diffraction patterns of Bi$_2$Se$_3$ samples quenched after treatment at a pressure of 7.7 GPa and heating at different temperatures. The structure of the reference sample is rhombohedral (Fig. 1, No 1). R$3m$, $a = 4.143$ Å, $c = 28.636$ Å, the cell parameters are the same as that of ICDD database PDF-2 [17]. The peaks in the diffraction patterns of samples, obtained at temperatures below 1173 K (Fig 1, No 2-4) were broad, indicating disorder or amorphization of the structure. After treatment at higher temperatures 1373 - 1473 K (Fig 1, No 6-7) the crystal structure became more ordered, these peaks are split and narrowed.

Since the diffraction peaks of the metastable phase of m-Bi$_2$Se$_3$ did not match to the high-pressure phase peaks obtained in the high-pressure diamond-anvil cell [5] we carried out a crystal-chemical analysis of the structures of all known sesquioxide chalcogenides with large size cations. Almost all sulphides and some selenides of rare-earth elements (RE) crystallize in the orthorhombic structure with the space group Pnma. Metastable phases with the orthorhombic structure Pnma were found after high pressures and high temperatures treatment of RE sulphides like Tm$_3$S with initial monoclinic P2$_1$/m structure [18]. The Pnma structure was previously detected in the metastable phase of Bi$_3$S$_3$ obtained after the treatment at lower pressures and temperatures [19] and in the present work at P = 4 GPa and T = 673 K. Here it should be mentioned, that after annealing at the temperature of 1200°C we observed transformation of the metastable high-pressure monoclinic phase m-Bi$_2$Se$_3$ into an orthorhombic phase with a Pnma structure. Thus we assumed that the structure of the new metastable
phase of m-Bi$_2$Se$_3$ would be similar to the monoclinic structure of thulium sulfide $P2_1/m$ and chose this structure as a prototype.

Figure 1. The evolution of Bi$_2$Se$_3$ X-ray data after HPHT treatment at a pressure of 7.7 GPa and temperatures: a) 1 - reference sample at ambient conditions; 2 – 473 K; 3 – 673 K; 4 – 873 K; 5 - 1173 K; 6 – 1373 K; 7 – 1473 K; (b) X-ray diffraction pattern of the sample No 3 (7.7 GPa and 673K) after Rietveld refinement. The grey line is the experimental data, black line is the calculated pattern (1). Ticks correspond to the 2 theta Bragg angles of m-Bi$_2$Se$_3$ (2). The bottom line is the difference pattern (3, exptl. – calcd.). The reliability parameter is equal $R_{Bragg}=18\%$.

The parameters of the unit cell and the coordinates of the atoms in the structure of the new phase (Fig.1, No. 3) with the space group $P2_1/m$ were obtained by the method of full-profile analysis by the use of FULLPROF program [21]. Here are its cell sizes: space group $P2_1/m$, $a=12.25(6)$Å, $b = 4.106(8)$ Å, $c = 11.49(7)$ Å, $\beta = 115.088^\circ$, $Z = 4$. The coordinates of 10 independent atoms are also defined. Thus, by quenching after HPHT treatment we obtained new metastable structures of m-Bi$_2$Se$_3$ ($P2_1/m$). The structure remains layered, but the interlayer distance decreased. The main difference is the decrease in the distance between metal atoms Bi-Bi 3.5-3.7Å.

Figure 2. Magnetic moment of m-Bi$_2$Se$_3$ sample (Fig. 1, No. 7) vs magnetic field at room temperature (a) and susceptibility vs magnetic field at $T = 100K$ and 300 K (b). Solid lines show Langevin fits.

The coordination numbers are 6, 7, 8. Coordinate polyhedrons of metal atoms form columns of
octahedral (BiSe₆) and mono- and double-capped trigonal prisms (BiSe₇ and BiSe₈) with the common ribs along the short axis "b". The interatomic distances of Bi-Bi in the $P2_1/m$ structure are much smaller than in the $Pnma$ structure. After the annealing of metastable phase at $T = 300 \, ^\circ C$ during 1 hour structure of the sample returned back into initial rhombohedral structure.

3.2. Magnetization

Magnetization versus magnetic field dependence of m-Bi₂Se₃ sample (Fig. 1a, No.7) shows general diamagnetic behavior with paramagnetic contribution (Fig. 2a). Fig. 2b displays the magnetic susceptibility with Langevin approximation. The approximation definitely shows the zero-field paramagnetic anomaly in the field less of about 2 kOe. Such an anomaly, a zero-field paramagnetic cusp, is typical for topological insulators [22].

The same cusp was observed in m-Sb₂Te₃ samples, as shown in Fig. 3a. In m-Sb₂Te₃ we observed superconductivity at $T=2K$ which was suppressed by low magnetic field as shown in Fig. 3b. While electrical and magnetic measurements clearly indicate transition into superconducting state, the DSC study did not show any peak in heat capacity at critical temperature. That may evidence two-dimensional character of superconductivity.

**Figure 3.** Magnetic susceptibility of m-Sb₂Te₃ phase vs magnetic field at $T=300K$ (a) and magnetic field effect on superconductivity transition temperature in m-Sb₂Te₃ phase (b)

**Figure 4.** Linear positive transverse magnetoresistance in polycrystalline metastable m-Bi₂Se₃ (Fig. 1, No. 7) (a) and m-Sb₂Te₃ phases (b).
Applying strong magnetic field at fixed temperatures T=1.8 and T=10 K we observed linear positive transverse magnetoresistance in metastable phase m-Bi$_2$Se$_3$ in strong magnetic field (Fig. 4a). In m-Sb$_2$Te$_3$ transverse magnetoresistance is positive and increases linearly with the magnetic field at H>25 kOe as shown in Fig. 4b.

4. Discussion
We synthesized new metastable phases m-Bi$_2$Se$_3$ and m-Sb$_2$Te$_3$, and determined the crystal structure of m-Bi$_2$Se$_3$ phase. Earlier superconductivity in high-pressure phases was observed "in situ" [4,5,8,9], but after the pressure release the structures transformed back into non-superconductive. The quenched metastable phase m-Sb$_2$Te$_3$ possess superconductivity transition at normal pressure. It is totally superconductive below T$_c$ = 1.75 K.

It should be noted, that the R(T) dependence in our case display not simply metallic behavior, it looks more likely as degenerated semiconductor. The linear magnetoresistance (LMR) effect in high fields (see Fig. 4) and the zero-field paramagnetic cusp (see Fig. 2b and 3a) are typical in the topological insulators. Both m-Bi$_2$Se$_3$ and m-Sb$_2$Te$_3$ have positive linear magnetoresistance at H>25 kOe. It should be mentioned, that the disorder in narrow-gap semiconductors also causes linear magnetoresistance [23], but a relatively narrow temperature range of superconductivity transition can indicate good degree of crystallinity in our case. Thus we believe that this effect as well as the zero-field paramagnetic cusp manifests a topological insulator state.

5. Conclusion
We synthesized bulk polycrystalline samples of new metastable phase of Bi$_2$Se$_3$ topological insulator using a high-pressure and high-temperature treatment at P = 7.7 GPa; T = 673-1473 K with the subsequent quenching and investigated their electrical and magnetic properties. The monoclinic phase has space group $P2_1/m$, and the unit cell parameters $a=12.25(6)$ Å, $b = 4.106$ (8) Å, $c = 11.49(7)$ Å, $\beta = 115.088^\circ$, $Z = 4$. We observed the linear positive transverse magnetoresistance effect and the zero-field paramagnetic cusp which are proper to topological insulators. Also we synthesized bulk polycrystalline samples of metastable at ambient conditions monoclinic (C2/m) phase of Sb$_2$Te$_3$. We observed superconductivity at T=2K in m-Sb$_2$Te$_3$. The critical current value of about 3 mA and an absence of the heat capacity peak at superconductivity transition indicate low-dimensional character of superconductivity in the case of m-Sb$_2$Te$_3$ phase.

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6. References
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