IOP Conference Series: Materials
Science and Engineering

PAPER • **OPEN ACCESS**

NMR studies of 3D topological insulators over a large temperature range

To cite this article: A O Antonenko *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **525** 012003

IOP Conf. Series: Materials Science and Engineering **525** (2019) 012003 doi:10.1088/1757-899X/525/1/012003

NMR studies of 3D topological insulators over a large temperature range

A O Antonenko[1], E V Charnaya[1], V V Marchenkov[2,3] and S V Naumov[2]

[1]Physics Department, St. Petersburg State University, 1 Ulyanovskaya Street, St. Petersburg, 198504, Russia
[2]M.N. Mikheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, 18 Sophya Kovalevskaya Street, Ekaterinburg, 620108, Russia
[3]Ural Federal University, 19 Mira Street, Ekaterinburg, 620002, Russia

E-mail: nastya5555@mail.ru

Abstract. Results of NMR measurements of the Bi2Te3 and Bi2Se3 3D topological insulators within the temperature range 11-293 K are presented. Two lines were demonstrated in the 125Te and 77Se spectra over the whole temperature range for single crystals in the c^B0 and c||B0 orientations as well as for Bi2Te3 and Bi2Se3 powders. The observed lines correlated to two non-equivalent positions of chalcogen atoms in the crystalline structure of investigated bismuth chalcogenides. The thermal activated character of charge carriers was found for the Bi2Te3 single crystal and powder. The activation energy was evaluated. It was shown for the Bi2Se3 powder that thermally activated charge carriers did not play the main role in conductivity. The nontrivial behaviour of the 125Te and 77Se NMR spectra for Bi2Te3 and Bi2Se3 single crystals in the orientation c||B0 was found at low temperatures which could not be explained by the orientation dependence of the line shapes and shifts in the topologically trivial semiconductors without structural phase transitions.

1. Introduction

Few years ago they started intensive studies of a new class of materials with nontrivial topology named “topological insulators” (TIs). The materials with unique properties, which appear due to topology of electron bands, were theoretically predicted by L. Fu and C. Kane in 2007 and later were experimentally found [1]. The nontrivial topology of electron bands in these materials emerges due to the strong spin-orbit coupling (SOC) and band inversion and is preserved by time reversal symmetry. It was shown that semiconductors like Bi_2Te_3 and Bi_2Se_3, which were earlier well known for their good thermoelectric properties, belonged to three-dimensional (3D) TIs. Such materials are considered as semiconductors or insulators, however, they show metallic surface conductivity. The electrons on the surface can move almost without any energy losses.

TIs bismuth chalcogenides with general formula $A_2^{V}B_3^{VI}$ are under enhanced attention of researchers due to their prospective applications in constructing elements and devices in different areas such as spintronics, magneto- and optoelectronics [2-4]. While the main properties of TIs are already confirmed, investigations of TIs are on the early stage of progress. Today there are only few studies of such TIs as Bi_2Te_3 and Bi_2Se_3 by nuclear magnetic resonance (NMR) [5-12].

This work reports the thermal evolution of the Bi_2Te_3 and Bi_2Se_3 properties over a large temperature range obtained by NMR.

2. Experiment

The Bi_2Te_3 and Bi_2Se_3 3D TIs were studied within a temperature range from 11.4 to 293 K using a Bruker Avance 400 NMR pulse spectrometer with the magnetic field 9.4 T. The high quality single crystals were grown by the Bridgman-Stockbarger method. The electrical resistance ratio at room and liquid helium temperatures, which characterizes the amount of lattice defects was equal to 25 for Bi_2Te_3 and 1.65 for Bi_2Se_3. Both crystals have the rhombohedral symmetry and the same layered crystal structure. The five individual atomic layers making up a quintuple layer lie in the sequence A1-Bi-A2-Bi-A1, where A1 and A2 denote the two different types of locations of chalcogen atoms (tellurium in case of Bi_2Te_3 or selenium in case of Bi_2Se_3). These atoms, A1 and A2, are crystallographically non-equivalent. The quintuple layers are coupled by the weak Van der Waals interaction. The layers are stacked along the ***c***-axis. The unit cell contains three formula units. The X-ray diffraction (XRD) method was used to control the sample orientation.

The temperature evolution of NMR spectra was studied for the powder samples and for thin single crystalline plates in two different orientations, in which the crystallographic ***c***-axis was parallel and perpendicular to the external magnetic field $\boldsymbol{B}_0$. Powder samples were obtained from the single crystals using mortar and pestle. The thickness of plates was 0.6 mm for Bi_2Te_3 and 3 mm for Bi_2Se_3.

To detect the NMR signals from ^{125}Te in Bi_2Te_3 and ^{77}Se in Bi_2Se_3 a spin-echo pulse sequence $\pi/2$-τ-π was applied. Because of very wide NMR lines and quite low natural abundance of ^{125}Te and ^{77}Se (near 7 % for both isotopes) the signals were bad enough. To improve the signal to noise ratio we used the number of scans in each experiment no less than 2^{11}. Two types of NMR spectra were collected. First, we found the intensities of the spin echo signals at various frequencies and plotted their envelope. Second, we summed up the echo data at stepped offset to get varied offset cumulative spectra (VOCS).

3. Results and discussion

3.1 Spectra at room temperature

The ^{125}Te spectra showed two lines at room temperature for all single crystalline and powder samples (figure 1). The ^{77}Se NMR spectra demonstrated clearly two lines only for the powder sample while only single lines were seen for the crystalline plates in both orientations because of low signal-to-noise ratio (figure 1).

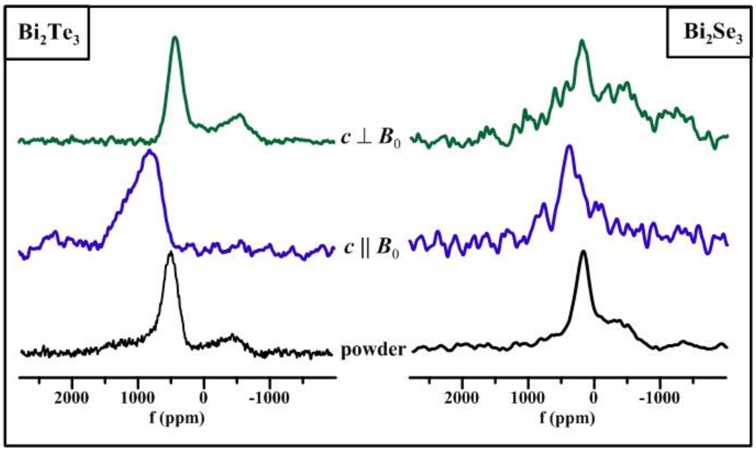

Figure 1. ^{125}Te (on the left) and ^{77}Se (on the right) VOCS for the Bi_2Te_3 and Bi_2Se_3 single crystals in two orientations and powders, respectively, at room temperature.

To explain the existence of these lines, simulations of the ^{125}Te and ^{77}Se powder NMR spectra were performed. The NMR data obtained for the Bi_2Te_3 and Bi_2Se_3 single crystals allowed us to calculate some parameters of the powder NMR spectra such as the isotropic shift δ_{iso}, anisotropy δ, and asymmetry η for the bismuth chalcogenides under study. We showed that the same values of these parameters could be found from the simulation of the powder NMR spectra. We demonstrated that the powder spectra could be deconvolved into two components (figure 2). The component intensity ratio was about 2:1 for the both compounds. In the crystallographic structure of the bismuth chalcogenides under study there are two non-equivalent crystallographic positions of chalcogen atoms. The amount of atoms in the A1 position is twice as much as in the A2 position. Using this and the results of the powder spectra simulation we could attributed the more intensive line to Te1 in Bi_2Te_3 and Se1 in Bi_2Se_3 and the less intensive one to Te2 in Bi_2Te_3 and Se2 in Bi_2Se_3. Earlier for nanoparticles of Bi_2Te_3 a little shoulder on the ^{125}Te NMR single line was shown [6]. This shoulder was treated as an influence of the sample surface.

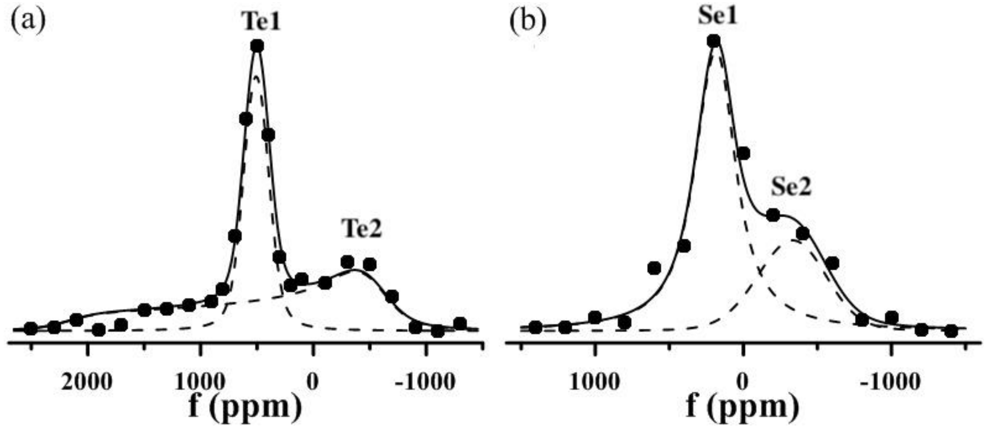

Figure 2. Deconvolution of the ^{125}Te (a) and ^{77}Se (b) NMR spectra at room temperature into two components (dashed lines) for the Bi_2Te_3 and Bi_2Se_3 powders, respectively. Solid lines – results of simulation of the powder NMR spectra, dots – experimental data from the envelope spectra.

3.2. Temperature evolution of the ^{125}Te NMR spectrum for Bi_2Te_3

We found almost the same behaviour of the ^{125}Te NMR spectra for the Bi_2Te_3 single crystal in the orientation $\boldsymbol{c}\perp\boldsymbol{B}_0$ and for powder with decreasing temperature. For both samples there was significant shift of the NMR lines to lower frequencies with decreasing temperature and the line width increased about two times (figure 3).

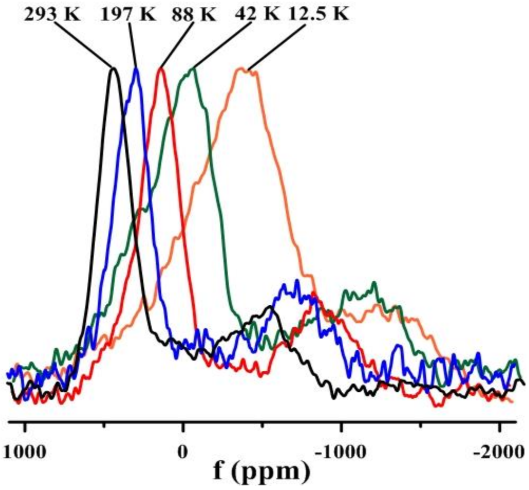

Figure 3. ^{125}Te VOCS for the Bi_2Te_3 single crystal in the orientation $\boldsymbol{c}\perp\boldsymbol{B}_0$ at different temperatures.

Using data obtained from the temperature evolution of the NMR spectra we can distinguish the contribution of the Knight shift to the total shift of NMR lines for both samples. It is known that for semiconductors the Knight shift has the following dependence on the charge carrier density n and temperature T [13]: $K_s \propto n/T$. For the intrinsic semiconductors this expression can be transformed into

$$K_s \propto \frac{n_0 e^{\frac{-E_a}{k_B T}}}{T} \tag{1}$$

where n_0 – charge carrier density in the high-temperature limit, E_a – activation energy and k_B – Bolzman constant.

The activation energies for charge carriers can be found using the temperature dependences of the Knight shift for Te1 and Te2 and the activation law (1). The values of E_a were the same for the single crystalline and powder samples and both lines within the framework of experimental error. The average value of the activation energy was 26 meV. It is one third of the energy gap for Bi_2Te_3 [14]. This means that the Fermi level in samples under study was shifted to the conduction band.

Extremely different situation was for single crystal Bi_2Te_3 in the orientation $\boldsymbol{c}||\boldsymbol{B}_0$. We found that the ^{125}Te NMR spectrum remained unchanged in general until 130 K. At lower temperatures the spectra changed drastically. The intensity of the line corresponded to Te2 increased significantly. At the lowest temperature this line became dominant (figure 4). Such inconsistency could not be caused by the orientation dependence for the topologically trivial semiconductor crystals without structural phase transition. Nowadays the nontrivial behaviour of the NMR spectra at low temperatures couldn't be explained within existing theoretical models because they do not take into account the strong SOC which plays the important role in TIs.

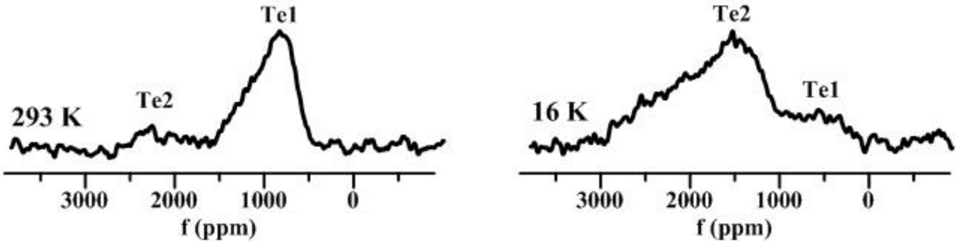

Figure 4. ^{125}Te VOCS for single crystal Bi_2Te_3 in the orientation $\boldsymbol{c}||\boldsymbol{B}_0$ at room temperature (on the left) and at the lowest measured temperature, 16 K, (on the right).

3.3. Temperature evolution of the ^{77}Se NMR spectrum for Bi_2Se_3

As Bi_2Se_3 studied had more defects which appeared during growing process than Bi_2Te_3 ($\rho_{293\,K}/\rho_{4.2\,K}$=1.65) we did not see such a pronounced shift of the ^{77}Se NMR spectra with decreasing temperature for the Bi_2Se_3 single crystal in the orientation $\boldsymbol{c}\perp\boldsymbol{B}_0$ and powder as it was for Bi_2Te_3 (figure 5). That means that charge carriers of defect nature play the main role in conductivity of Bi_2Se_3. However, for single crystalline Bi_2Se_3 in the orientation $\boldsymbol{c}||\boldsymbol{B}_0$ we observed the nontrivial behaviour of ^{77}Se NMR spectra at low temperatures similar to that observed for bismuth telluride.

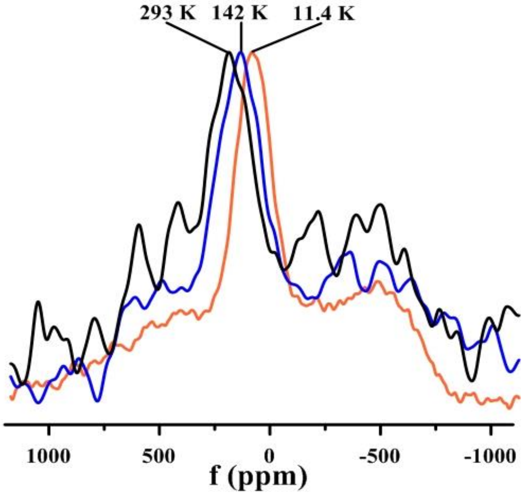

Figure 5. ^{77}Se VOCS for the Bi_2Se_3 single crystal in the orientation $\boldsymbol{c}\perp\boldsymbol{B}_0$ at different temperatures.

4. Conclusions

It was found that the ^{125}Te and ^{77}Se NMR spectra over the temperature range 11.4-293 K were generally consisted of two lines attributed to Te1 and Te2 in Bi_2Te_3 and Se1 and Se2 in Bi_2Se_3 for all samples studied. It was observed almost the same temperature evolution of ^{125}Te NMR spectra for the Bi_2Te_3 single crystal in the orientation $\boldsymbol{c}\perp\boldsymbol{B}_0$ and powder. The shift of NMR lines was determined mainly by the Knight shift. It was demonstrated the thermal activation character of charge carriers for the Bi_2Te_3 samples and the activation energy was found. It was shown that charge carriers of defect nature played the main role in conductivity for the Bi_2Se_3 single crystal in the orientation $\boldsymbol{c}\perp\boldsymbol{B}_0$ and powder. For bismuth chalcogenides single crystals in the orientation $\boldsymbol{c}||\boldsymbol{B}_0$ the abnormal behaviour of the ^{125}Te and ^{77}Se NMR spectra was discovered. This anomaly can not be explained within the framework of existing theoretical models.

Acknowledgments

The studies were supported by RFBR, grant 19-57-52001. NMR and XRD measurements were carried.

References

[1] Fu L and Kane C L 2007 Topological insulators with inversion symmetry *Phys. Rev. B* **76** 045302

[2] Hasan M Z and Kane C L 2010 Colloquium: Topological insulators *Rev. Mod. Phys.* **82** 3045-67

[3] Scanlon D O, King P D C, Singh R P, De la Torre A, Walker S McK, Balakrishnan G, Baumberger F and Catlow C R A 2012 Controlling bulk conductivity in topological insulators: key role of anti-site defects *Adv. Mater.* **24** 2154-8

[4] Olbrich P, Golub L E, Herrmann T, Danilov S N, Plank H, Bel'kov V V, Mussler G, Weyrich Ch, Schneider C M, Kampmeier J, *et al*. 2014 Room-temperature high-frequency

transport of dirac fermions in epitaxially grown Sb_2Te_3-and Bi_2Te_3-based topological insulators *Phys. Rev. Lett*. **113** 096601

[5] Taylor R E, Leung B, Lake M P and Bouchard L-S 2012 Spin-lattice relaxation in bismuth chalcogenides *Phys. Chem. C* **116** 17300-5

[6] Koumoulis D, Chasapis T C, Taylor R E, Lake M P, King D, Jarenwattananon N N, Fiete G A, Kanatzidis M G and Bouchard L-S 2013 NMR probe of metallic states in nanoscale topological insulators *Phys. Rev. Lett.* **110** 026602

[7] Georgieva N M, Rybicki D, Guehne R, Williams G V M, Chong S V, Kadowaki K, Garate I and Haase J 2016 ^{77}Se nuclear magnetic resonance of topological insulator Bi_2Se_3 *Phys. Rev. B* **93** 195120

[8] Levin E M, Riedemann T M, Howard A, Jo N H, Bud'ko S L, Canfield P C and Lograsso T A 2016 ^{125}Te NMR and Seebeck effect in Bi_2Te_3 synthesized from stoichiometric and Te-rich melts *Phys. Chem. C* **120** 25196-202

[9] Podorozhkin D Yu, Charnaya E V, Antonenko A, Mukhamad'yarov R, Marchenkov V V, Naumov S V, Huang J C A, Weber H W and Bugaev A S 2015 Nuclear magnetic resonance study of a Bi_2Te_3 topological insulator *Phys. Solid State* **57** 1741-5

[10] Antonenko A O, Charnaya E V, Nefedov D Yu, Podorozhkin D Yu, Uskov A V, Bugaev A S, Lee M K, Chang L J, Naumov S V, Perevozchikova Yu A, *et al.* 2017 NMR studies of single crystals of the topological insulator Bi_2Te_3 at low temperatures *Phys. Solid State* **59** 855-9

[11] Antonenko A O, Charnaya E V, Nefedov D Yu, Podorozhkin D Yu, Uskov A V, Bugaev A S, Lee M K, Chang L J, Naumov S V, Perevozchikova Yu A, *et al.* 2017 NMR study of topological insulator Bi_2Te_3 in a wide temperature range *Phys. Solid State* **59** 2331-9

[12] Antonenko A O, Nefedov D Y, Charnaya E V, Naumov S V and Marchenkov V V 2018 ^{77}Se low-temperature NMR in the Bi_2Se_3 single crystalline topological insulator *Appl. Magn. Reson.* **49** 599-605

[13] Selbach H, Kanert O and Wolf D 1979 NMR investigation of the diffusion and conduction properties of the semiconductor tellurium. I. Electronic properties *Phys. Rev. B* **19** 4435

[14] Yavorsky B Yu, Hinsche N F, Mertig I and Zahn P 2011 Electronic structure and transport anisotropy of Bi_2Te_3 and Sb_2Te *Phys. Rev. B* **84** 165208

out in the Research park of St. Petersburg State University.