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

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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 Bi²Te³ and Bi²Se³, 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 A²V₃B₆VI 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 Bi²Te³ and Bi²Se³ by nuclear magnetic resonance (NMR) [5-12].

This work reports the thermal evolution of the Bi²Te³ and Bi²Se³ properties over a large temperature range obtained by NMR.
2. Experiment
The Bi$_2$Te$_3$ and Bi$_2$Se$_3$ 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$_2$Te$_3$ and 1.65 for Bi$_2$Se$_3$. 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$_2$Te$_3$ or selenium in case of Bi$_2$Se$_3$). 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 $B_0$. Powder samples were obtained from the single crystals using mortar and pestle. The thickness of plates was 0.6 mm for Bi$_2$Te$_3$ and 3 mm for Bi$_2$Se$_3$.

To detect the NMR signals from $^{125}$Te in Bi$_2$Te$_3$ and $^{77}$Se in Bi$_2$Se$_3$ a spin-echo pulse sequence $\pi/2-\tau-\pi$ 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$_2$Te$_3$ and Bi$_2$Se$_3$ single crystals in two orientations and powders, respectively, at room temperature.](image-url)
To explain the existence of these lines, simulations of the $^{125}\text{Te}$ and $^{77}\text{Se}$ powder NMR spectra were performed. The NMR data obtained for the Bi$_2$Te$_3$ and Bi$_2$Se$_3$ single crystals allowed us to calculate some parameters of the powder NMR spectra such as the isotropic shift $\delta_{\text{iso}}$, anisotropy $\delta$, and asymmetry $\eta$ 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$_2$Te$_3$ and Se1 in Bi$_2$Se$_3$ and the less intensive one to Te2 in Bi$_2$Te$_3$ and Se2 in Bi$_2$Se$_3$. Earlier for nanoparticles of Bi$_2$Te$_3$ a little shoulder on the $^{125}\text{Te}$ NMR single line was shown [6]. This shoulder was treated as an influence of the sample surface.

![Figure 2](image.png)

**Figure 2.** Deconvolution of the $^{125}\text{Te}$ (a) and $^{77}\text{Se}$ (b) NMR spectra at room temperature into two components (dashed lines) for the Bi$_2$Te$_3$ and Bi$_2$Se$_3$ 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 $^{125}\text{Te}$ NMR spectrum for Bi$_2$Te$_3$

We found almost the same behaviour of the $^{125}\text{Te}$ NMR spectra for the Bi$_2$Te$_3$ single crystal in the orientation $c \perp B_0$ 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).
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]:

\[
K_s \propto \frac{n_0 e^{-E_a/k_B T}}{T}
\]  

(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\(_2\)Te\(_3\) [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\(_2\)Te\(_3\) in the orientation \( c \parallel B_0 \). 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.
3.3. Temperature evolution of the $^{77}$Se NMR spectrum for Bi$_2$Se$_3$

As Bi$_2$Se$_3$ studied had more defects which appeared during growing process than Bi$_2$Te$_3$ ($\rho_{293\, K}/\rho_{4.2\, K}=1.65$) we did not see such a pronounced shift of the $^{77}$Se NMR spectra with decreasing temperature for the Bi$_2$Se$_3$ single crystal in the orientation $c \perp B_0$ and powder as it was for Bi$_2$Te$_3$ (figure 5). That means that charge carriers of defect nature play the main role in conductivity of Bi$_2$Se$_3$. However, for single crystalline Bi$_2$Se$_3$ in the orientation $c || B_0$ 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$_2$Se$_3$ single crystal in the orientation $c \perp B_0$ at different temperatures.](image)

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$_2$Te$_3$ and Se1 and Se2 in Bi$_2$Se$_3$ for all samples studied. It was observed almost the same temperature evolution of $^{125}$Te NMR spectra for the Bi$_2$Te$_3$ single crystal in the orientation $c \perp B_0$ 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$_2$Te$_3$ 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$_2$Se$_3$ single crystal in the orientation $c \perp B_0$ and powder. For bismuth chalcogenides single crystals in the orientation $c || B_0$ 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.

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