CONDENSED MATTER

## Temperature Studies of Raman Spectra in MnBi<sub>2</sub>Te<sub>4</sub> and MnSb<sub>2</sub>Te<sub>4</sub> Magnetic Topological Insulators

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Received July 25, 2023; revised August 8, 2023; accepted August 8, 2023

Raman spectra of magnetic topological crystalline insulators in a wide temperature range including the magnetic ordering region are studied in detail. The anharmonicity parameters and Grüneisen mode parameters of Raman-active phonons in the studied crystals have been determined. It has been shown that the temperature dependence of the frequency of the  $A_{lg}^{(1)}$  (~48 cm<sup>-1</sup>) phonon in MnBi<sub>2</sub>Te<sub>4</sub> coincides within ±0.1 cm<sup>-1</sup> with the standard anharmonic model disregarding the spin–phonon coupling. The polarization dependences of Raman spectra in the MnSb<sub>2</sub>Te<sub>4</sub> crystals indicate that Sb and Mn atoms are strongly mixed in them unlike the isostructural MnBi<sub>2</sub>Te<sub>4</sub> crystals.

**DOI:** 10.1134/S0021364023602543

The formation of the magnetic order in quantum functional materials provides a wide platform to study fundamental spin phenomena, e.g., in strongly correlated materials [1], multiferroics [2], and recently discovered magnetic topological materials [3–5]. These materials are promising for application in spintronics, magnetic memory devices, and quantum information technologies.

The introduction of magnetism in topological insulators breaks the time reversal symmetry, and the magnetic exchange interaction opens a gap in surface topological states, which are gapless in the absence of this interaction. This can lead to various new topological quantum states such as the quantum anomalous Hall effect or an axion insulator state. Doping with magnetic atoms and magnetic proximity effects are natural methods to introduce magnetism into non-magnetic topological insulators. The quantum anomalous Hall effect was experimentally implemented in a Cr-doped (Bi, Sb)<sub>2</sub>Te<sub>3</sub> topological insulator film only at low temperature below 30 mK [6] because the mag-

netic gap varied irregularly along the sample surface due to the inhomogeneous distribution of magnetic atoms [7].

The implementation of the first intrinsic antiferromagnetic topological insulator  $MnBi_2Te_4$  with a Néel temperature of 25.4 K [4] demonstrated a new and efficient method to introduce magnetism into topological insulator with a large magnetic gap and uniform magnetic order. This opens good prospects for potential applications in low-power electronics, as well as for further studies of the quantum anomalous Hall effect and new topological states such as axion insulator states, at higher temperatures.

Layered MnBi<sub>2</sub>Te<sub>4</sub> and MnSb<sub>2</sub>Te<sub>4</sub> crystals undergo transitions to antiferromagnetic and ferromagnetic states, respectively, at temperatures of  $\sim 25-30$  K and are the first experimental implementations of the intrinsic magnetic order in three-dimensional topological insulators. Since the interlayer magnetic order in these materials is closely related to the band topol-



**Fig. 1.** (Color online) X-ray diffraction patterns of the studied (bottom)  $MnBi_2Te_4$  and (top)  $MnSb_2Te_4$  crystals shifted along the vertical axis for clarity.

ogy, this can provide new efficient ways to the coupling between the interlayer exchange and other microscopic degrees of freedom.

The aims of this work are to study in detail Raman spectra of magnetic topological crystalline insulators in a wide temperature range including the magnetic ordering region, to determine the anharmonic parameters of the studied crystals, and to examine the possible effect of the spin-phonon coupling on the phonon frequencies [8, 9].

The studied MnBi<sub>2</sub>Te<sub>4</sub> and MnSb<sub>2</sub>Te<sub>4</sub> single crystals were  $\sim 50-100$ -µm-thick plates with sizes up to several millimeters. The technology for growth of MnBi<sub>2</sub>Te<sub>4</sub> single crystals was described in detail in [4, 10]. MnSb<sub>2</sub>Te<sub>4</sub> single crystals were grown using the same technology with somewhat different growth parameters. Figure 1 presents diffraction patterns obtained for the samples of both compounds on a BRUKER XRD D2 Phaser X-ray diffractometer (Cu  $K_{\alpha 1}$  radiation,  $5^{\circ} < 2\Theta < 100^{\circ}$ ). The EVA and TOPAS-4.2 software packages were used to determine the phase composition of the samples and to perform their structural analysis. The recorded diffraction patterns exactly correspond to the calculated ones and confirm the tetradymite structure  $R\overline{3}m$  of both compounds. The quality of the recorded diffraction patterns for the studied MnSb<sub>2</sub>Te<sub>4</sub> samples is noticeably higher than that recently reported for this compound in [11].

We studied the Raman spectra of the  $MnBi_2Te_4$ and  $MnSb_2Te_4$  crystals excited by the 632.817-nm radiation of a HeNe laser. Laser radiation with a power below ~10 mW was focused onto a spot ~100 µm in diameter on a uniform region of the sample surface. Such a power density did not change Raman spectra at



Fig. 2. (Color online) Raman spectra of the  $MnBi_2Te_4$  crystal measured at temperatures (solid line) 4.2, (dashed line) 50, and (dotted solid line) 295 K and shifted along the vertical axis for clarity.

any exposure times, which could be varied from several to 30 minutes to record spectra. The samples were placed in an optical helium cryostat, where the temperature can be varied from 4.2 K to room temperature with an accuracy of ~0.1 K. Raman spectra were recorded in the direction close to the perpendicular to the sample surface using a DilorXY 500 Raman spectrograph equipped with a cooled CCD detector.

Some Raman spectra of the MnBi<sub>2</sub>Te<sub>4</sub> crystals recorded at various temperatures are shown in Fig. 2. Lines caused by scattering of light on various Ramanactive optical phonons are seen in these spectra. The temperature dependence of the frequency of the lowest-frequency (~27 cm<sup>-1</sup>)  $E_g^{(1)}$  Raman-active mode, which was theoretically predicted in [10], was reliably identified and measured for the first time.

In this work, we carefully measured the temperature dependence of the frequency of the  $A_{lg}^{(1)}$  phonon marked by an arrow in Fig. 2. It is well known [12] that the temperature dependence of the phonon frequencies  $\omega(T)$  from liquid-helium to room temperatures,

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which is due to anharmonicity, can be well described by the following formula including three-phonon interactions:

$$\omega(T) = \omega_0 + \delta \omega \left[ 1 + \frac{2}{\exp(\hbar \omega_0 / 2k_{\rm B}T) - 1} \right].$$
(1)

Here,  $\omega_0$  and  $\delta\omega$  are certain frequency constants such that  $\omega_0 + \delta\omega$  is the phonon frequency at zero temperature and the ratio  $\delta\omega/\omega_0$  determines the slope of an almost linear dependence  $\omega(T)$  at high temperatures, and  $\hbar$  and  $k_B$  are the reduced Planck and Boltzmann constants, respectively. In the presence of a sufficiently strong spin-phonon coupling, the temperature dependence of the phonon frequency  $\omega(T)$  at temperatures below the magnetic ordering temperature can generally deviate from Eq. (1).

The authors of [8] stated that the frequency of the  $A_{lg}^{(1)}$  (~48 cm<sup>-1</sup>) phonon in the MnBi<sub>2</sub>Te<sub>4</sub> crystals at temperatures below the transition temperature to the antiferromagnetic state is ~0.3 cm<sup>-1</sup> higher than that given by Eq. (1). They attributed this excess to the spin—phonon coupling, which is maximal for this phonon according to their calculations. On the contrary, a decrease in the frequency of this phonon by approximately the same value was observed experimentally in [9]. We note that such small deviations of the frequency of the  $A_{lg}^{(1)}$  phonon from the standard anharmonic behavior require the determination of the frequency with a very high accuracy. Meanwhile, the accuracy of determining the  $A_{lg}^{(1)}$  phonon frequency in [8, 9] was at the limit of the experimental capabilities, exceeding in particular the spectral resolution, which was no less than ~0.5 cm<sup>-1</sup>.

One of the main factors determining the accuracy of the frequency determined by the mathematical processing of the recorded experimental spectra is their quality, i.e., a high ratio of a Raman signal intensity to noise. At the same time, a large data acquisition time is required to achieve a high signal-to-noise ratio in an experiment because the intensity of the Raman spectra of the studied  $MnBi_2Te_4$  crystals is not high. As a result, a long-term, even weak, instability of the calibration of spectral instruments can be manifested during this time, which can in turn introduce an additional error in the determined phonon frequency in experiments at various temperatures.

We carefully measured the Raman spectra of the MnBi<sub>2</sub>Te<sub>4</sub> crystals at temperatures from liquid helium to room temperature and determined the spectral positions of Raman bands with a high accuracy at a spectral resolution  $\leq 0.5$  cm<sup>-1</sup>. To increase the accuracy of determining phonon frequencies, light from a calibration low-pressure neon lamp with the intensity comparable with the Raman intensity was sent to the optical path of the setup simultaneously with the



**Fig. 3.** (Color online) (Circles with error bars) temperature dependence of the frequency of the  $A_{lg}^{(1)}$  phonon in the MnBi<sub>2</sub>Te<sub>4</sub> crystals. The solid line is the best fit of Eq. (1) with the parameters  $\omega_0 \approx 48.4 \text{ cm}^{-1}$  and  $\delta \omega \approx -0.094 \text{ cm}^{-1}$  to the experimental data.

recording of the Raman spectra. Thus, the light of the calibration lamp consisting of the known narrow lines that is measured simultaneously with the studied Raman spectrum allowed us to significantly increase the accuracy of determining phonon frequencies using the appropriate mathematical processing.

The frequency of the maximum of the Raman band on the  $A_{lg}^{(1)}$  phonon thus determined at various temperatures in a wide range including the magnetic ordering region is shown by circles with error bars in Fig. 3, where the solid line is the best fit of Eq. (1) with the parameters determined by the least squares method to the experimental data. The inset of Fig. 3 shows the same results in the low-temperature region in more detail. It is seen that the temperature dependence of the frequency of the  $A_{lg}^{(1)}$  (~48 cm<sup>-1</sup>) phonon in MnBi<sub>2</sub>Te<sub>4</sub> coincides within ±0.1 cm<sup>-1</sup> with the standard anharmonic model disregarding the spin– phonon coupling. This means that the estimates obtained in [8, 9] for the spin–phonon coupling are not accurate or at least are ambiguous.

We measured the temperature dependences of the frequencies of all Raman modes detected in the  $MnBi_2Te_4$  crystals, which allowed us to determine the anharmonicity parameters of various modes; they are summarized in Table 1. It is seen that relative changes  $|\Delta\omega|/\omega$  in the frequencies of all modes under the variation of the temperature from liquid helium to

room are very close to each other except for the  $A_{lg}^{(1)}$  phonon for which this parameter is somewhat smaller. In addition, the relative change in the frequency of the

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| Mode              | $\omega$ (5 K),<br>cm <sup>-1</sup> | <i>d</i> ω/ <i>dp</i> , [13]<br>cm <sup>-1</sup> /GPa | $\gamma_i$ | $\frac{10^3  \Delta \omega  / \omega}{\Delta T} = 290 \text{ K}$ |
|-------------------|-------------------------------------|---|------------|--|
| $E_{g}^{(1)}$     | 28.1                                | -   | -          | 41 ± 5   |
| $A_{ m lg}^{(1)}$ | 48.3                                | 1.44  | 1.52       | $31 \pm 2$   |
| $E_{g}^{(2)}$     | 69.8                                | _   | _          | $36 \pm 3$   |
| $E_{g}^{(3)}$     | 107.9                               | 1.63  | 0.77       | $37 \pm 3$   |
| $A_{ m lg}^{(2)}$ | ~118                                | —   | _          | $38 \pm 8$   |
| $A_{lg}^{(3)}$    | 144.6                               | 1.94  | 0.68       | 39 ± 5   |

Table 1. Anharmonic parameters of the MnBi<sub>2</sub>Te<sub>4</sub> crystals

 $A_{lg}^{(2)}$  phonon was determined with a large error because this phonon is manifested in Raman spectra only as a shoulder of the strongest  $E_g^{(3)}$  mode in the Raman spectra (see Fig. 4).



Fig. 4. (Color online) Polarized Raman spectra of the  $MnBi_2Te_4$  crystals at temperatures (bottom panel) 297 and (top panel) 4.2 K measured at the polarization of the exciting laser radiation  $E_1$  (solid lines) parallel and (dotted lines) perpendicular to the polarization of scattered light  $E_{Rs}$ , which is parallel to the surface of the sample. Arrows mark six Raman-active modes.

The Grüneisen parameters also characterize the anharmonicity of phonons in crystals. Table 1 presents the Grüneisen parameters of various modes calculated as  $\gamma_i = (B/\omega_i)(d\omega_i/dp)$ , where B = 51 GPa is the bulk modulus and the derivatives  $d\omega_i/dp$  are determined from the data reported in [13].

To verify the correctness of the identification of the observed Raman modes, we measured Raman spectra at different linear polarizations  $\mathbf{E}_{l}$  and  $\mathbf{E}_{Rs}$  of the exciting laser radiation and scattered light, respectively. The paramagnetic MnBi<sub>2</sub>Te<sub>4</sub> bulk crystals belong to the space group  $R\overline{3}m$  with the point symmetry group  $D_{3d}$  at the  $\Gamma$  point of the Brillouin zone. They exhibit six Raman modes including three  $A_{1g}$  modes and three double degenerate  $E_{g}$  modes [8, 9, 14]. Measurements of polarized Raman spectra can be used to identify these modes of different symmetries having different selection rules. In particular, the  $E_g$  modes have nonzero diagonal and off-diagonal components of the Raman tensor and can thereby be detected at both the aligned and crossed polarizations  $E_{l}$  and  $E_{Rs}$ . As seen in Fig. 4, the  $A_{1g}$  modes are observed only at the aligned polarizations  $\mathbf{E}_{l} \parallel \mathbf{E}_{Rs}$  and are absent in Raman spectra recorded at  $\mathbf{E}_1 \perp \mathbf{E}_{Rs}$ . Since the Raman tensor in MnBi<sub>2</sub>Te<sub>4</sub> in the magnetically ordered phase is the same as that in the nonmagnetic one [15], the same picture is also observed at low temperatures (see the upper panel of Fig. 4).

MnSb<sub>2</sub>Te<sub>4</sub> single crystals are complete crystalline analogs of MnBi<sub>2</sub>Te<sub>4</sub> single crystals and also should exhibit six Raman modes (three  $E_g$  modes and three  $A_{\rm lg}$  modes). According to our calculations similar to those previously performed for MnBi<sub>2</sub>Te<sub>4</sub> [10], the frequencies of  $E_g$  and  $A_{1g}$  Raman modes in MnSb<sub>2</sub>Te<sub>4</sub> are 29, 94, and 123 cm<sup>-1</sup> and 52, 136, and 167 cm<sup>-1</sup>, respectively. However, any reliable detection of all six modes and, the more so, their symmetry identification are still absent. Figure 5 presents the polarized Raman spectra of the MnSb<sub>2</sub>Te<sub>4</sub> crystals recorded at low and room temperatures and at the aligned and crossed polarizations  $\mathbf{E}_{l}$  and  $\mathbf{E}_{Rs}$ . It is seen that four different modes with frequencies of ~90, 119, 139, and 264  $cm^{-1}$ can be identified at room temperature. Comparing these frequencies with the calculated ones, the 90- and 119-cm<sup>-1</sup> modes can be attributed to  $E_g$  modes, whereas the 139-cm<sup>-1</sup> mode can be interpreted as an  $A_{1g}$  mode. At the same time, the frequency of the highest-frequency mode  $\sim 264 \text{ cm}^{-1}$  is much higher than the upper limit of possible frequencies of the vibrational modes in MnSb<sub>2</sub>Te<sub>4</sub>, as clearly seen from the calculated phonon density of states projected on each atom shown in Fig. 6.

Furthermore, according to Fig. 5, the intensities' of all observed bands are hardly dependent on the mutual orientation of the polarization  $E_1$  and  $E_{Rs}$ . A similar

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Fig. 5. (Color online) Polarized Raman spectra of the  $MnSb_2Te_4$  crystals at temperatures (bottom panel) 297 and (top panel) 8 K measured at the polarization of the exciting laser radiation  $E_1$  (solid lines) parallel and (dotted lines) perpendicular to the polarization of scattered light  $E_{Rs}$ , which is parallel to the surface of the sample.



Fig. 6. (Color online) Density of states that is obtained with the calculated phonon band structure of  $MnSb_2Te_4$  and is projected on the (solid line) Te, (dashed line) Sb, and (dotted line) Mn atoms.

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picture is also observed at the low temperature (see the upper panel of Fig. 5).

The comparison of the polarized Raman spectra shown in Figs. 4 and 5 certainly indicates that the symmetry of the  $MnSb_2Te_4$  crystals is broken. This breaking can possibly be due to the significant mixing of Sb and Mn atoms in crystals  $MnSb_2Te_4$  [11] in contrast to the isostructural crystals  $MnBi_2Te_4$ , which can just explain the observed properties of the polarized Raman spectra shown in Fig. 5.

To summarize, the detailed studies of the Raman spectra of  $MnBi_2Te_4$  magnetic topological crystalline insulators in a wide temperature range from 4.2 to 300 K have been performed to determine the anharmonic parameters of various phonon modes. It has been found that, in contrast to the results reported in [8, 9], the temperature dependence of the frequency of the  $A_{lg}^{(1)}$  (~48 cm<sup>-1</sup>) phonon in MnBi<sub>2</sub>Te<sub>4</sub> can be described within ±0.1 cm<sup>-1</sup> with the standard anharmonic model given by Eq. (1) disregarding the spin–

monic model given by Eq. (1) disregarding the spinphonon coupling. The Raman spectra of the  $MnSb_2Te_4$  crystals recorded at the aligned and crossed polarizations  $E_1$  and  $E_{Rs}$  of the exciting laser radiation and scattered light, respectively, indicate that Sb and Mn atoms are strongly mixed in these crystals.

## FUNDING

This work was supported by the Azerbaijan Ministry of Science and Education (program "Development of the Preparation Technology of Multifunctional Convertors Based on Nanostructures"). E.V.C. acknowledges the support of St. Petersburg State University (project no. 94031444).

## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Translated by R. Tyapaev