Occupancy Disorder in Magnetic Topological Insulators Studied by X-ray Diffraction

Laura Christina Folkers[1,2,3] , Anna Isaeva[3,4]

1: Institute for Solid State and Materials Physics, TU Dresden, Germany;
2: Leibniz Institute for Solid State and Materials Research, Dresden, Germany;
3: ct.qmat, Cluster of Excellence for Complexity and Topology in Quantum Matter;
4: University of Amsterdam, Amsterdam, The Netherlands

Magnetic topological insulators (MTIs) are a hot topic of materials science, promising future availability of spintronics with low energy consumption, quantum computing and phenomena like the Quantized Anomalous Hall Effect (QAHE) [1-2]. MTIs are chemically and structurally akin to the original non-magnetic topological insulators. Of those, the tetradymites Bi_2Te_3 and Sb_2Te_3 have recently proven to allow the introduction of a third magnetic element resulting in magnetically active, topologically non-trivial compounds. A magnetic element can be incorporated either via substitution on the Bi/Sb position in $(Bi, Sb)_2Te_3$, or by adding a third element which introduces a new crystallographic site, resulting for example in $MnBi_2Te_4$. $(Bi, Sb)_2Te_3$ itself and all members of its family exhibit the rhombohedral $R\bar{3}m1$ space group (No. 166) [2]. Therein interchanging sheets of Mn, (Bi, Sb) and Te build septuple layers with the central sheet being Mn (Wyckoff position 3a). Situated between the respective layers is a van der Waals gap (Fig. 1).

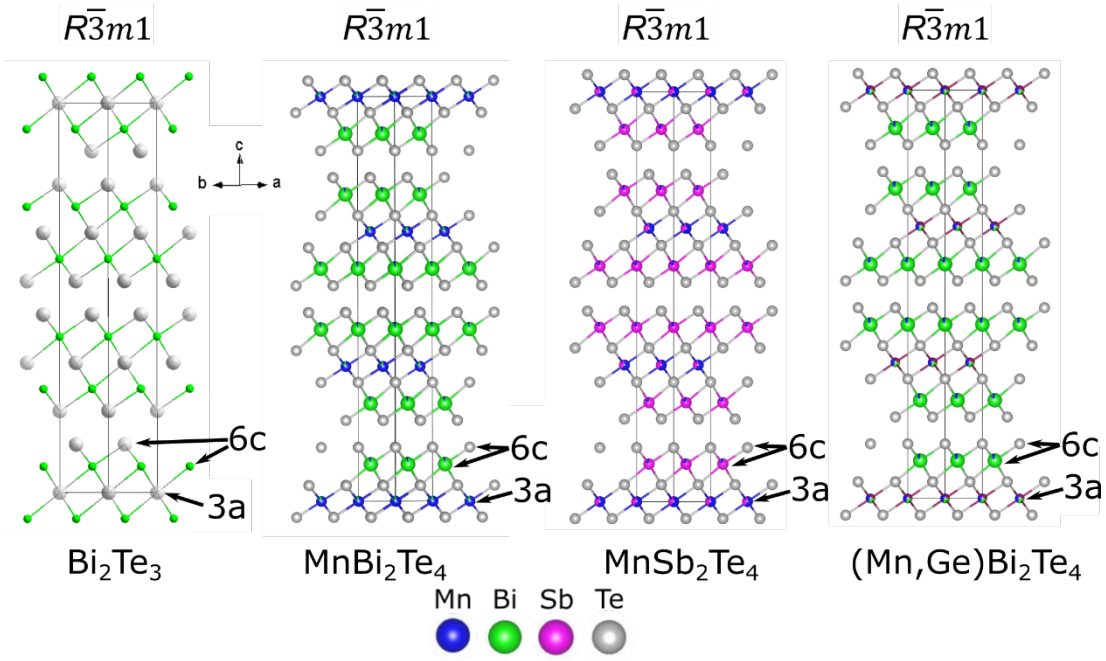

Figure 1: The structure of Bi2Te3 [3], MnBi2Te4, MnSb2Te4 and (Mn, Ge)Bi2Te4. All of those compounds are classified as topological insulators and are currently being investigated by us.

Investigating new analogues of $MnBi_2Te_4$ is important not only to find IMTIs that exhibit higher critical temperatures and are fully ferromagnetic with a high net magnetization, but also to fundamentally explore the existence of other variances of topological and magnetic order. While new analogues can be found by testing other p-elements than Bi and other magnetic elements than Mn, the structure – property relationships are scrutinized by precise crystallographic and magnetic studies. From there we strive for insight into the connection between varying occupancies and bond lengths and different forms of magnetism.

Single crystal diffraction experiments of $MnBi_2Te_4$ [2,4] reproducibly exposed intermixing of Mn and Bi ($Mn_{0.86(2)}Bi_{1.90(7)}Te_{4.00(6)}$ [preliminary EDX data], $Mn_{0.85(3)}Bi_{2.10(3)}Te_4$ [4]) in our data, as well as in

several studies by other groups ($MnBi_{2.14}Te_{3.96}$ [5], $Mn_{1.01}Bi_{1.99}Te_4$ and $Mn_{0.98}Bi_{2.05}Te_4$ [6]). Magnetic measurements consistently showed antiferromagnetically coupled layers of ferromagnetically ordered sheets of Mn, stacked along the *c*-axis.

Exchanging Bi for Sb, we found that $MnSb_2Te_4$ is also a synthetically achievable compound. Similar to $MnBi_2Te_4$, $MnSb_2Te_4$ features intermixing of Mn and Sb ($Mn_{0.79(6)}Sb_{2.27(4)}Te_{4.00(2)}$ [preliminary EDX data], $Mn_{0.9}Sb_{2.3}Te_4$ [7]) and first results point at it being a soft ferromagnet with $T_C \sim 30K$. Intriguingly, a recent study by Murakami *et al.* finds polycrystalline $MnSb_2Te_4$ to be ferrimagnetic with $T_C = 25K$ due to a certain amount of the magnetic Mn occupying the position of the non-magnetic Sb [8].

These compounds are known to react sensitively to synthesis procedure and tempering history. Hence, our studies aim at understanding the greater connection between synthesis aspects and the resulting structural and physical properties. More precisely we studied $MnBi_2Te_4$ and $MnSb_2Te_4$ containing various amounts of Mn and other analogues of these systems. In these studies we uncovered, that the magnetism in $MnSb_2Te_4$ is even more sensitive to annealing procedures than previously expected.

In an attempt to understand how diluting the amount of magnetic moments in the structure affects the compound, we prepared $Mn_{(1-x)}Ge_xBi_2Te_4$, where Ge is non-magnetic. Successful single crystal syntheses allowed for a primary structural refinement, uncovering a distribution of Mn, Ge and Bi over all possible positions. Preliminary magnetic measurements on a crystalline sample show that the Néel temperature of $Mn_{0.38(1)}Ge_{0.45(3)}Bi_{2.16(1)}Te_{4.00(2)}$ (preliminary EDX data) is 11K, approximately half of T_N of $MnBi_2Te_4$.

References

[1] Y. Ando, *Journal of the Physical Society of Japan*, **(2013)**, *82*, 102001

[2] M. M. Otrokov, I. I. Klimovskikh, H. Bentmann, et al., *Nature*, **(2019)**, *576*, 416-422.

[3] Y. Feutelais, B. Legendre, N. Rodier, V. Agafonov, *Materials Research Bulletin*, **(1993)**, *28*, 591-596

[4] A. Zeugner, F. Nietschke, A. U. B. Wolter, et al., *Chemistry of Materials*, **(2019)**, *31*, 2795-2806.

[5] H. Li, S. Liu, C. Liu, et al., *Physical Chemistry Chemical Physics*, **(2020)**, *22*, 556-563.

[6] M.-H. Du, J. Yan, V. R. Cooper, M. Eisenbach, *Advanced Functional Materials*, **(2020)**, 2006516.

[7] L. Zhou, Z. Tan, D. Yan, et al., *Physical Review B*, **(2020)**, *102*, 85114.

[8] T. Murakami, Y. Nambu, T. Koretsune, et al., *Physical Review B*, **(2019)**, *100*, 195103.