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Occupancy Disorder in the Magnetic Topological Insulator Candidate Mn$_{1-x}$Sb$_{2+x}$Te$_4$

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Abstract: MnSb$_2$Te$_4$ is a candidate magnetic topological insulator exhibiting more pronounced cation intermixing than its predecessor MnBi$_2$Te$_4$. Investigating the cation intermixing and its possible implications on the magnetic order in MnSb$_2$Te$_4$ are currently hot topics in research on quantum materials for spintronics and energy-saving applications.

Two single-crystal X-ray diffraction measurements of Mn$_{1-x}$Sb$_{2+x}$Te$_4$ ($x = 0.06$ and $x = -0.1$) are presented alongside a detailed discussion of its crystal structure with a spotlight on the apparent occupancy disorder between the two cations. This disorder has been noted by other groups as well, yet never been analyzed in-depth with single-crystal X-ray diffraction. The latter is the tool of choice to receive a meaningful quantification of antisite disorder. Between the two synthesis procedures we find subtle differences in phases and/or alternation of the cation content which has implications on the magnetic order, as illustrated by bulk magnetometry. Understanding and assessing this disorder in magnetic topological insulators of the Mn$X_2$Te$_4$ ($X = $ Bi, Sb) type is crucial to gauge their applicability for modern spintronics. Furthermore, it opens new ways to tune...
the "chemical composition – physical property" relationship in these compounds, creating an alluring aspect also for fundamental science.

**Keywords:** Single Crystals, Magnetic Topological Materials, Disorder, X-ray Diffraction, Magnetism

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1 Powder Diffraction

1.1 Sample 1

Fig. 1: Powder diffraction measurement of Sample 1, exhibiting the full range of measurement with a zoomed fraction of the most intense peaks in the upper right corner. The black line shows measured intensities, the red line depicts calculated intensities (Le Bail method) and the blue line is their difference. Green vertical tick marks indicate the peak positions of MnSb$_2$Te$_4$. 
Table 1: Lattice parameters and space group of MnSb$_2$Te$_4$ as refined from the powder diffraction data displayed in Fig S1.

| Phase     | Space Group | Lattice Parameters          |
|-----------|-------------|-----------------------------|
| MnSb$_2$Te$_4$ | $R\bar{3}m$ | $a = 4.2326(1)$ Å, $c = 40.870(1)$ Å |
1.2 Sample 2

Fig. 2: Full range of the powder diffraction measurement of Sample 2 with a zoomed inset. The upper black line shows the measured diffraction pattern, the red line indicates the calculated pattern (Le Bail method), the lower blue line indicates the difference and the vertical tick marks indicate the reflex positions. In this case the key to the various contributing phases is shown in the legend to the upper left.

Figures 1 and 2 display the powder diffraction patterns of Sample 1 and Sample 2. As discussed in the main text, S2 is a phase mixture containing MnSb$_2$Te$_4$ (ca. 90%) as a main phase, Mn doped Sb$_2$Te$_3$ (ca. 6%) as a second most intense phase and some smaller amounts of MnSb$_4$Te$_7$ (ca. 4%). Phase fractions are estimated.
from a very preliminary Rietveld refinement without cationic intermixing. In this refinement we were able to vary the atomic coordinates and the isotropic displacement factors for the main phase MnSb$_2$Te$_4$. The starting values for the atomic positions were taken from Reference [9] and the isotropic displacement parameters ended up in the region of $U \approx 0.1 \, \text{Å}^2$. For the side phases Sb$_2$Te$_3$ and MnSb$_4$Te$_7$ the atomic positions could be carefully varied, but the isotropic displacement parameters had to be fixed to $U = 0.1 \, \text{Å}^2$. As a result we received the following statistical factors: $R_p \approx 12\%$; GOF $\approx 3$; $R_{obs} \approx 13-20\%$. The Mn doping in Sb$_2$Te$_3$ was established from EDX data showing crystalline pieces that contain around 2 at% of Mn.

## 2 Additional Crystallographic Data for Sample 1 and Sample 2

### 2.1 Sample 1

| Atom | x          | y          | z          | SOF          |
|------|------------|------------|------------|--------------|
| Mn1  | 0.333333   | 0.666667   | 0.09165(2) | 0.188(3)     |
| Sb1  | 0.333333   | 0.666667   | 0.09165(2) | 0.811(3)     |
| Mn2  | 1          | 0          | 0          | 0.74(1)      |
| Sb2  | 1          | 0          | 0          | 0.28(1)      |
| Te1  | 0.666667   | 0.333333   | 0.04094(2) | 1            |
| Te2  | 0          | 1          | 0.13120(2) | 1            |

Table 3: Refined atomic coordinates of sample 1 and respective site occupancy factor (SOF).
| Atom | \( U_{11} \) | \( U_{22} \) | \( U_{33} \) | \( U_{12} \) | \( U_{13} \) | \( U_{23} \) |
|------|-------------|-------------|-------------|-------------|-------------|-------------|
| Mn1  | 0.0164(3)   | 0.0164(3)   | 0.0281(5)   | 0.0082(2)   | 0           | 0           |
| Sb1  | 0.0164(3)   | 0.0164(3)   | 0.0281(5)   | 0.0082(2)   | 0           | 0           |
| Mn2  | 0.0193(6)   | 0.0193(6)   | 0.0202(8)   | 0.0096(3)   | 0           | 0           |
| Sb2  | 0.0193(6)   | 0.0193(6)   | 0.0202(8)   | 0.0096(3)   | 0           | 0           |
| Te1  | 0.0169(3)   | 0.0169(3)   | 0.0201(3)   | 0.0085(1)   | 0           | 0           |
| Te2  | 0.0162(3)   | 0.0162(3)   | 0.0242(4)   | 0.0081(1)   | 0           | 0           |

Table 4: Anisotropic atomic displacement parameters (in \( \text{Å}^2 \)) of atoms in sample 1.

### 2.2 Sample 2

| Atom | \( x \)   | \( y \)   | \( z \)   | SOF |
|------|-----------|-----------|-----------|-----|
| Mn1  | 0.333333  | 0.666667  | 0.09208(4)| 0.152(6) |
| Sb1  | 0.333333  | 0.666667  | 0.09208(4)| 0.848(6) |
| Mn2  | 1         | 0         | 0         | 0.64(2) |
| Sb2  | 1         | 0         | 0         | 0.37(2) |
| Te1  | 0         | 1         | 0.13169(3)| 1   |
| Te2  | 0.666667  | 0.333333  | 0.04147(2)| 1   |

Table 5: Refined atomic coordinates of sample 2 and respective site occupancy factor (SOF).

| Atom | \( U_{11} \) | \( U_{22} \) | \( U_{33} \) | \( U_{12} \) | \( U_{13} \) | \( U_{23} \) |
|------|-------------|-------------|-------------|-------------|-------------|-------------|
| Mn1  | 0.0182(5)   | 0.0182(5)   | 0.0305(7)   | 0.0091(2)   | 0           | 0           |
| Sb1  | 0.0182(5)   | 0.0182(5)   | 0.0305(7)   | 0.0091(2)   | 0           | 0           |
| Mn2  | 0.02(2)     | 0.02(2)     | 0.03(2)     | 0.008(9)    | 0           | 0           |
| Sb2  | 0.02(2)     | 0.02(2)     | 0.02(1)     | 0.011(7)    | 0           | 0           |
| Te1  | 0.0165(4)   | 0.0165(4)   | 0.0221(6)   | 0.0082(2)   | 0           | 0           |
| Te2  | 0.0164(4)   | 0.0164(4)   | 0.0179(6)   | 0.0082(2)   | 0           | 0           |

Table 6: Anisotropic atomic displacement parameters (in \( \text{Å}^2 \)) of atoms in sample 2.
Fig. 3: Reconstructed reciprocal space image in the hk1 layer. The reflexes highlighted with green circles violate the rhombohedral reflection condition $-h+k+l=3n$. Due to this reflection condition no reflexes of the main individual are expected to be present in this layer. Therefore we can conclude, that these reflections stem from the second twin individual.
3 MnBi$_2$Te$_4$ Single Crystal Refinement

| Refined composition | Mn$_{0.93(3)}$Bi$_{2.07(3)}$Te$_4$ |
|---------------------|----------------------------------|
| Formula weight $M_r$ (g/mol) | 992.8                            |
| Crystal size (mm$^3$) | 0.05 x 0.05 x 0.001               |
| Color               | Metallic grey                    |
| Crystal system      | Rhombohedral                     |
| Space group         | $R3m$                            |
| Lattice Parameters (Å) | $a = b = 4.3311(1), c = 40.897(1)$ |
| Cell angles         | $\alpha = \beta = 90^\circ, \gamma = 120^\circ$ |
| Formula units (Z)   | 3                                |
| $R_{int}$ (%)       | 5.7                              |
| $R_{obs}$ (%)       | 4.60                             |
| $wR_{obs}$ (%)      | 14.88                            |
| GOF(all)            | 1.96                             |
| Max. residual density (e $\times 10^{-6}$ pm$^{-3}$) | 6.13 |
| Min. residual density (e $\times 10^{-6}$ pm$^{-3}$) | -7.20 |
| No. of parameters   | 14                               |
| No of constraints   | 2                                |
| No. of unique reflections | 833                              |
| 2Theta max.         | 46.39                            |
| 2Theta min.         | 2.99                             |
| CCDC no.            | 2107054                          |

Table 7: Data collection values and structural information for MnBi$_2$Te$_4$.

| Atom | x          | y          | z            | SOF  |
|------|------------|------------|--------------|------|
| Mn1  | 0.333333   | 0.666667   | 0.09168(2)   | 0.054(8) |
| Bi1  | 0.333333   | 0.666667   | 0.09168(2)   | 0.946(8) |
| Mn2  | 1          | 0          | 0            | 0.820(9) |
| Bi2  | 1          | 0          | 0            | 0.180(9) |
| Te1  | 0          | 0          | 0.13352(2)   | 1    |
| Te2  | 0.666667   | 0.333333   | 0.03934(2)   | 1    |

Table 8: Refined atomic coordinates and site occupancy factors (SOF) of MnBi$_2$Te$_4$. 
Table 9: Anisotropic atomic displacement parameters (in Å²) of atoms in MnBi₂Te₄.

| Atom | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|------|------|------|------|------|------|------|
| Mn₁  | 0.0183(2) | 0.0183(2) | 0.0251(3) | 0.00913(9) | 0     | 0     |
| Bi₁  | 0.0183(2) | 0.0183(2) | 0.0251(3) | 0.00913(9) | 0     | 0     |
| Mn₂  | 0.0184(6) | 0.0184(6) | 0.0213(9) | 0.0092(3)  | 0     | 0     |
| Bi₂  | 0.0184(6) | 0.0184(6) | 0.0213(9) | 0.0092(3)  | 0     | 0     |
| Te₁  | 0.0177(3) | 0.0177(3) | 0.0202(3) | 0.0089(1)  | 0     | 0     |
| Te₂  | 0.0200(3) | 0.0200(3) | 0.0172(3) | 0.0100(1)  | 0     | 0     |

The here discussed MnBi₂Te₄ sample was prepared via a standard solid state route from the binary precursors MnTe and Bi₂Te₃ mixed in a 0.81:1.00 MnTe:Bi₂Te₃ ratio. For annealing the sample was placed into the hot oven at 650°C, which was programmed to cool to 590°C after 24h with the rate of 1K/h. However due to some problems with oven control the sample was later cooled down to 574°C before it was quenched into water. Powder diffraction of the resulting compound revealed MnBi₂Te₄ to be the main phase, with Bi₂Te₃ as a second strongest phase. The measurement was performed on a Malvern Panalytical XPERT PRO diffractometer in Bragg Brentano geometry, equipped with a copper X-ray source and a PIXcel detector.

Single crystal XRD suitable samples could be picked and were measured on a Bruker Kappa APEX II diffractometer, equipped with a Molybdenum X-ray source and the APEX II detector. Indexing, integration and refinement were done with the software discussed in the experimental part of the main text. Refinement results are displayed in Table 7.