



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

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- 1st March for experiments carried out up until June of the previous year;
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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: “Time and temperature dependent single-crystal diffraction on multinary antimony tellurides including element contrast enhancement by resonant scattering”	Experiment number: HS-4363
Beamline: ID11	Date of experiment: from: 21.07.2011 to: 26.07.2011	Date of report: 29.11.2012
Shifts: 15	Local contact(s): Loredana Erra	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Prof. Dr. Oliver Oeckler* (Leipzig University and Ludwig Maximilian University, Munich) M. Sc. Philipp Urban* (Leipzig University) M. Sc. Simon Welzmler* (Leipzig University) M. Sc. Felix Fahrnbauer* (Leipzig University)		

Report:

Aim

Resonant scattering experiments are essential to determine the element distribution if neither conventional X-rays nor neutrons provide sufficient scattering contrast.^[1] This is the case for germanium antimony tellurides (GST materials), where the electron counts of Sb and Te differ by just one and thus have very similar atomic form factors. Substitution with indium or tin aggravates this problem. As GST materials are widely used as phase-change materials^[2] and in addition have intriguing thermoelectric properties,^[3] insight into structural details is required in order to understand how these properties are affected by the chemical surrounding of the atoms or building blocks.^[4]

The combination of resonant diffraction at the K absorption edges of In, Sn, Sb and Te (29.2 – 31.8 keV) with *in-situ* heating experiments is the method of choice to elucidate diffusion phenomena and phase transitions which occur in these materials at about 300 °C.^[5]

Experiments and Results

In one part of the experiments, high-resolution diffraction data of model crystals with well-known structures were measured in order to obtain reliable dispersion correction terms $\Delta f''$ and $\Delta f'''$ via the Kramers-Kronig transform from fluorescence data. Corresponding values from various sources (e.g. NIST,^[6] Henke^[7] and CROSEC^[8] database) are often not accurate enough near the absorption edges because they are calculated theoretically for the pure elements and do not take into account the chemical environment of the compounds investigated. We used high quality crystals of SnSe₂, CrSbSe₃, PbTe, InSeI, SnTe and Sb₂Te₃ as reference compounds in order to compare various approaches and to obtain refined values from “calibration crystals” that can be used as constants in refinements of related compounds. Dispersion correction terms were refined with JANA2006^[9] and compared with the theoretical ones and those calculated from fluorescence spectra (cf. Tab. 1).

Tab.1: Comparison between some $\Delta f'$ correction terms from different sources.

Compound	Element	Energy / keV	NIST	CROSSEC	Fluorescence	Refinement
InSeI	In	27.932	-5.52	-7.30	-6.96	-7.14 (3)
SnSe ₂	Sn	29.195	-5.46	-7.63	-6.56	-7.05 (9)
CrSbSe ₃	Sb	30.466	-5.52	-6.91	-6.24	-7.06 (4)
PbTe	Te	31.808	-5.39	-7.62	-6.28	-8.22 (15)

With these insights it was possible to reliably refine the structures of single crystals of $\text{Ge}_3\text{Sb}_{\sim 0.6}\text{In}_{\sim 1.4}\text{Te}_6$, $\text{Ge}_{1.3}\text{Sn}_{0.7}\text{Sb}_2\text{Te}_5$, $\text{Ge}_{0.6}\text{Sn}_{0.4}\text{Sb}_2\text{Te}_4$ and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ with multiple datasets at the corresponding absorption edges and far from them with no constrained site occupancies. Additionally, *in-situ* temperature-dependent diffraction experiments at the absorption edge of Sb revealed reversible structural changes in the crystal structure of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ($P\bar{3}m1$, $a = 4.2257(2)$ Å, $c = 17.2809(18)$ Å, $R1 = 0.037$; cf. Fig. 1).

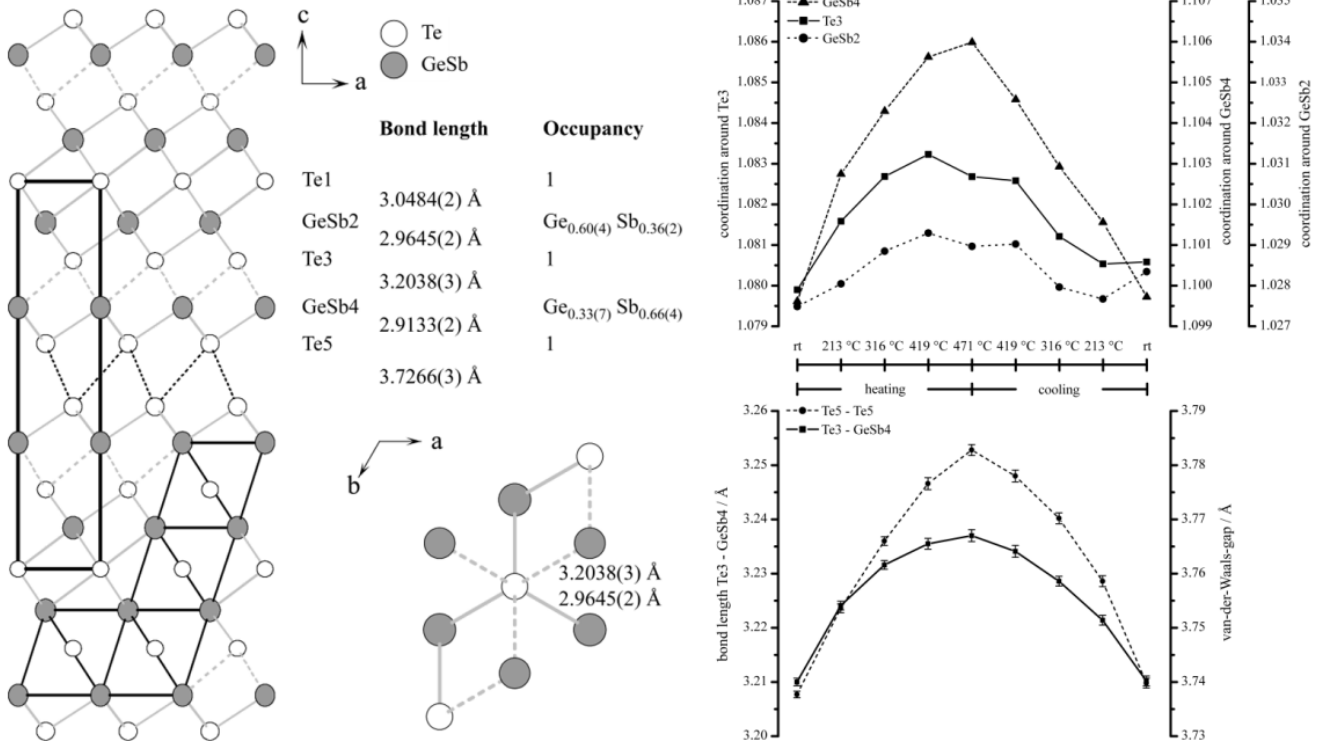


Fig. 1: Crystal structure of $\text{Ge}_2\text{Sb}_2\text{Te}_5$. Left: crystal structure at room temperature. A unit cell and the (pseudo)octahedral coordination are outlined. Middle: bond lengths, site occupancies and pseudooctahedral coordination around Te3. Top right: the regularity of the octahedral coordination decreases reversibly with increasing temperature. Bottom right: a GeTe-type layer detaches reversible from the block.

These experiments prove the element distribution unambiguously. Joint refinements of multiple datasets outline the importance of reliable dispersion correction terms. In most cases, fluorescence data are an excellent source for $\Delta f'$.

In further experiments, we obtained diffraction data from disordered compounds $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)$ with $4 \leq n \leq 17$. Datasets were collected at room temperature near the absorption edges of Sb and Te, so that joint refinements of the average structure ($Fm\bar{3}m$, $a \approx 6.00$ Å) were possible. The real structure is characterized by cation defect short-range order in finite defect layers combined with local distortions, which leads to diffuse streaks in the diffraction patterns. Reconstructed undistorted reciprocal space volumes allowed us to extract the intensity distribution along these streaks and thus to develop a disorder model that clearly relates the features present in the diffuse scattering to certain structural features. A comparison between experimental and simulated data is shown in Fig. 2.

The intensity distribution in these diffuse streaks was tracked *in-situ* until the high-temperature phase emerges at ~ 500 °C. At elevated temperatures, we observed an intermediate phase that corresponds to a trigonal superstructure of the NaCl type (cf. Fig. 2, right). This structure is long-range ordered as it lacks diffuse scattering; however, it is not thermodynamically stable compared to the trigonal layered structures which can be observed at room temperature.

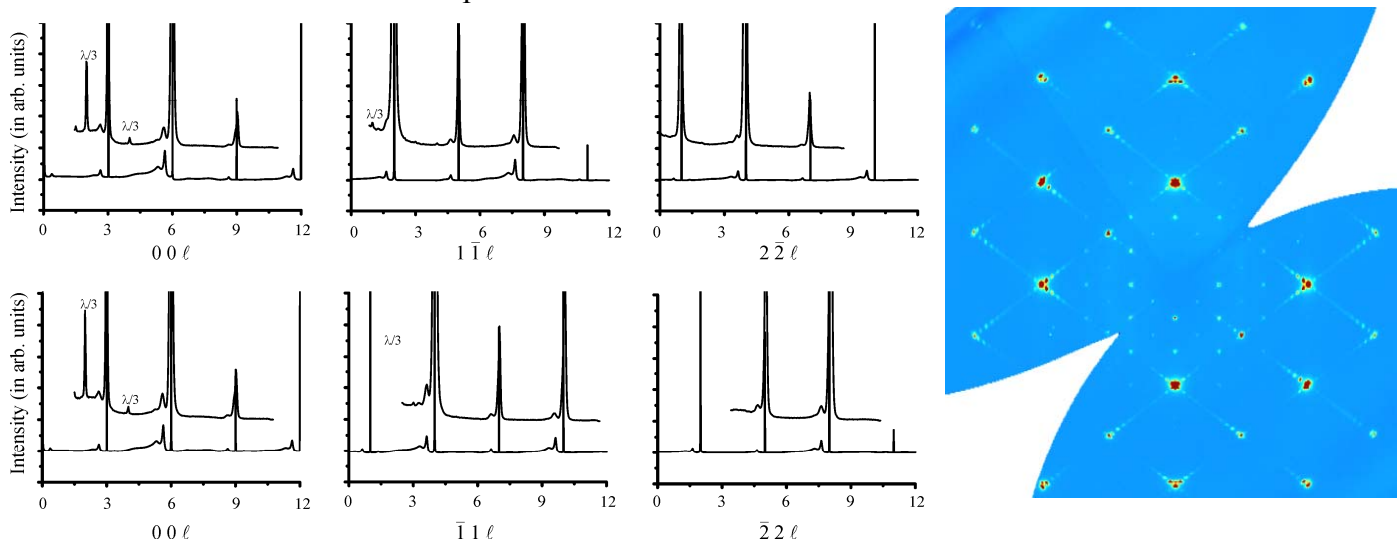


Fig. 2: Left: experimental diffuse streaks along $00\ell_t$ (the equal directions $-\ell_t = \ell_t$ are both depicted to corroborate the symmetry expected for this streak), and $1\bar{1}\ell_t / \bar{1}1\ell_t$ as well as $2\bar{2}\ell_t / \bar{2}2\ell_t$ ($\ell_t > 0$) of a crystal with the composition $(\text{GeTe})_6\text{Sb}_2\text{Te}_3$ (top histogram in each graph) in comparison to corresponding simulated intensities (bottom histogram in each graph), $\lambda/3$ reflections (observed due to the high beam intensity) are indicated. Right part: Diffraction pattern of the intermediate-temperature phase of a crystal with the composition $(\text{GeTe})_9\text{Sb}_2\text{Te}_3$.

Concluding, the mechanism of the phase transitions involves two parts: cation diffusion and a rearrangement of the anion substructure. These two parts of the phase transition are somehow independent and do not occur at the same time and/or temperature. Measurements at ID11 were very successful, and a large amount of data could be collected efficiently. The beamline proved ideal for our purposes.

Outlook

The data obtained demonstrate the potential of the method and allowed us to investigate the element distribution in multinary antimony tellurides at various temperatures. The results will be published soon, and will yield several papers. In addition, *in-situ* investigations allow drawing qualitative conclusions of the temperature dependent changes in the crystal structure. The experience gained concerning the influence of beam energy, measurement strategies and appropriate temperature and time regimes makes it easy to obtain high-quality data for future problems.

References

- [1] J.-L. Hodeau, V. Favre-Nicolin, S. Bos, H. Renevier, E. Lorenzo, J.-F. Berar, *Chem. Rev.* **2001**, *101*, 1843. [2] M. Wuttig, N. Yamada, *Nat. Mater.* **2007**, *6*, 824. [3] T. Rosenthal, M. N. Schneider, C. Stiewe, M. Döblinger, O. Oeckler, *Chem. Mater.* **2011**, *23*, 4349. [4] M. N. Schneider, T. Rosenthal, C. Stiewe, O. Oeckler, *Z. Kristallogr.* **2010**, *225*, 463. [5] M. N. Schneider, X. Biquard, C. Stiewe, T. Schröder, P. Urban, O. Oeckler, *Chem. Commun.* **2012**, *48*, 2192. [6] C. T. Chantler, *J. Phys. Chem. Ref. Data* **1995**, *24*, 71. & C. T. Chantler, *J. Phys. Chem. Ref. Data* **2000**, *29*, 597. [7] B. L. Henke, E. M. Gullikson, J. C. Davis, *At. Data Nucl. Data Tables* **1993**, *54*, 181. [8] D. T. Cramer, D. A. Libermann, *J. Chem. Phys.* **1970**, *53*, 1891. & D. T. Cromer, D. A. Libermann, *Acta Crystallogr. Sect. A* **1981**, *37*, 267. [9] V. Petricek, M. Dusek, L. Palatinus, JANA2006, Prague, **2006**.