7. Background of Research

This project investigated the fundamental mechanism in materials for state-of-the-art data storage devices. Such devices, like the digital versatile disc (DVD), are of huge technological importance and understanding their properties greatly benefits information technology. The recording layer of these devices contains so-called phase-change materials (PCM). The name arises from the fact that they can switch reversibly between a well-ordered, crystalline phase, and a disordered, amorphous phase. Binary information is stored in these layers in form of crystalline and amorphous dots, which encode the states '0' and '1', respectively. The resulting high contrast in the materials' properties of these two states (e.g. concerning the optical permittivity) is exploited to encode binary data. But even despite their huge technological importance, the underlying physics of the actual phase-change process remained foggy to the present day.

A prominent difficulty in this question is concerns the atomic-scale structure of the phases participating in the phase-change process. Both of these phases need to be elucidated to understand the process. Whereas this has successfully been done for the crystalline phase for a number of PCMs, the amorphous phase is much more difficult to explore. Though an amorphous compound lacks the long-range order (i.e. an order that basically affects all atoms) found in crystals, it possesses a short-range order, or SRO (i.e. affecting only direct atomic neighbours) and an intermediate-range order, or IRO (i.e. affecting clusters of atoms). These subtle interactions are difficult to determine, and have only recently been discussed for the 'traditional' phase-change materials being composed of germanium, antimony and tellurium (GeSbTe materials).

A first model for phase-change process in the prototypical PCM $Ge_2Sb_2Te_5$ (which is used in the DVD-RW) was proposed by Kolobov et al. [1], explaining the material characteristics by taking into account the different local environments of the SRO of the Ge atoms in the crystalline and in the amorphous phase. A number of experimental as well as theoretical investigations followed, which have been summarized in a review by Wuttig and Yamada [2]. They discuss basic characteristics of PCMs and alternative models for the phase-change mechanism. However, the importance of structural order beyond individual atomic environments was emphasized in the theoretical works of Huang and Robertson [3]. They revealed that differences in the intermediate range order (or IRO) are the principal reason for the optical contrast, which is the fundamental property for the actual application as PCM. Their findings were later confirmed experimentally by Shportko and coworkers [4], who describe that 'resonant bonds' on an IRO level are responsible for the extreme differences in the optical properties. The IRO, which can be thought of as the relative arrangement of individual local building blocks (e.g. bonding polyhedra), is difficult to determine with typical experimental or theoretical approaches. One of the few methods of choice is Anomalous X-ray scattering (AXS).

A new class of PCM, which was recently proposed as the next generation of data storage materials [5,6], is possesses the composition $(GeTe)_{1-x}$-$(CuTe)_x$ or GeCuTe in the following. In comparison with GeSbTe materials, these compositions show a remarkable different behavior concerning PCM properties like the optical contrast, while at the same time retaining an appropriate performance for data storage applications. The optical contrast, for instance, is given by the difference of the optical permittivities of the crystalline and of the amorphous phase, ε_∞(cryst.) and ε_∞(amorph.), respectively. It is known that in GeSbTe, ε_∞(cryst.) remains constant irrespective of the GeTe content, whereas ε_∞(amorph.) is increasing for lower contents of GeTe. The opposite trend is observed in GeCuTe, where ε_∞(cryst.) decreases strongly and ε_∞(amorph.) remains nearly constant with decreasing content of GeTe. Both trends lead to a reduction of the optical contrast when the GeTe content is reduced, but in the case of the GeCuTe, the different trends even lead to a negative optical contrast for larger CuTe contents – i.e. the amorphous phase is actually more reflective than the corresponding crystalline phase. Other properties, like the thermal stability of the amorphous phase, given by the temperature of crystallization, also show distinctly different trends.

Understanding the origins of these trends will help provide a basis to verify or to revise the current phase-change models. Therefore, precise data on the structure of the amorphous compounds both on the short- and the intermediate-range order level are necessary. This project was thus aimed to investigate the structure of the new phase-change material class GeCuTe.

[1] Kolobov, A. V., Fons, P., Frenkel, A. I., Ankudinov, A. I. , Tominaga, J., Uruga, T. (2004). Nat. Mater. **3**, 703-708.

[2] Wuttig, M., Yamada, N. (2007). Nat. Mater. 6, 824-832.

[3] Huang, B. and Robertson, J. (2010). Phys. Rev. B 81, 081204(R).

[4] Shportko, K., Kremers, S., Woda, M., Lencer, D., Robertson, J., Wuttig, M. (2008). Nat. Mater. 7, 653-658.

[5] Saito, Y., Sutou, Y., Koike, J. (2014): J. Phys. Chem. C 118, 26973-26980.

[6] Jóvári, P., Sutou, Y., Kaban, I., Saito, Y., Koike, J. (2013): Scr. Mater. 68, 122-125.

8. Research methodology

Conventional structural characterization of materials employs diffraction of X-rays from a sample material. In the case of crystalline matter, a characteristic pattern ('Bragg peaks') is produced, from which the periodic arrangement of the atoms in the crystal can be reconstructed. On the other hand, disordered materials like chalcogenide glasses lack the long-range correlations found in crystals and thus generally only produce broad and weak signals in the diffraction pattern. Nonetheless, these information can be used to interpret the structure as an average arrangement of atoms and their mutual correlations.

The determination of the microscopic structure in disordered materials is still a challenging task, and therefore this project relied on the research possibilities offered by modern third generation synchrotron facilities like SPring-8/Japan or the ESRF/France. An accurate structural description can be obtained by a comprehensive approach that combines information provided by different techniques. These synchrotron methods include mainly x-ray absorption fine structure (XAFS) and anomalous x-ray scattering. Both techniques provide element-specific information, but XAFS is more suitable to study the immediate vicinity of each element, called the short-range order. On the other hand, it is known that amorphous compounds, especially chalcogenide glasses like GeCuTe, exhibit an order on the scale of larger distances, which is the intermediate-range order. The IRO comprises correlated arrangements of atoms beyond their nearest neighbours, e.g. the connection between individual building blocks like bonding polyhedra. This distance scale can be probed by AXS measurements, which thus constitute a key role for the structural determination. The combined results of these methods can be used in a subsequent Reverse Monte Carlo Simulation (RMC), which simulates a model of the real-space structure based on the experimental reference data. More accurately, RMC uses an ensemble of particles which are randomly moved in a simulation box until sufficient agreement simultaneously with all experimental data is achieved. Further details on this procedure are outlined e.g. in references [7, 8].

[7] Hosokawa, S., Stellhorn, J., Pilgrim, W.-C. (2015): Mater. Res. Soc. Symp. Proc. 1757, mrsf14-1757-uu06-05.
[8] Stellhorn, J. R., Hosokawa, S., Pilgrim, W.-C. (2014): Z. Phys. Chem. **228**, 1005-1032.

9. Results/impacts

My studies investigate the local atomic order of GeCuTe comprehensively. Together with my advisor in this project, Prof. Hosokawa, various materials were analyzed and the results were published in scientific journals as listed below in section 11. My most recent publication reveals the structure of the amorphous phase of Cu_2GeTe_3. The results are based on the analysis of experimental data from AXS and XAFS, modeled by RMC, as described above. The extensive experimental approach represents a distinct improvement compared to previous experimental findings, which were limited to the SRO and were not able to explain the fast phase-change process in this material or its' peculiar properties. I was able to present a model for the structure of the amorphous phase of Cu_2GeTe_3, which is considered to be the most promising material in the GeCuTe system for the creation of a next-generation data storage device. This material was observed to possess superior properties compared to current phase-change memories (e.g. the DVD or Blu-Ray disk, based on GeSbTe materials).

My new study combines different experimental inputs to achieve an unprecedentedly detailed view on the structure. The information is used to explain the fast phase-change mechanism in Cu_2GeTe_3 from a point of view of the local structure, and show in detail the differences and similarities to the crystalline phase, and the important role of Cu atoms for the fast phase transition. It is for example confirmed that smaller ring structures and a large number of homopolar bonds are formed, in agreement with previous theoretical studies. It is also found that during the phase-change process, especially Cu atoms tend to move towards the centers of the 6-fold rings of the crystal, thereby forming new bonds and resulting in a broader distribution of ring structures, but also preserving some structural motifs of the crystal. This information supports the understanding of the excellent material properties and will advance the research for new data-storage devices.

(Note that this publication is not yet published. Currently, it is under review in *Physical Review Letters*. The manuscript is attached to this report.)

10. Research Presentations during the period of the fellowship (Name of the conference, title, place, date)

- **SRI 2018**, International Conference on Synchrotron Radiation Instrumentation 2018, Taipei, Taiwan (Jun 2018) “Anomalous X-ray Scattering Experiments for Disordered Materials at the SAGA Light Source“

- **JSSRR 2018**, Meeting of the Japanese Society for Synchrotron Radiation Research, Tsukuba, Japan (Jan 2018) "A structural study of the rejuvenation effect in amorphous Gd-Co metal by Anomalous X-ray Scattering"

- **ISS2017**, International Symposium on Superconductivity, Tokyo, Japan (Dec 2017) "An x-ray fluorescence holographic study on a Fe-based high-temperature superconductor $FeSe_{0.4}Te_{0.6}$"

- **ALC17**, Atomic Level Characterization, Lihue, USA (Dec 2017) "Valence-selective x-ray fluorescence holography: an example of an yttrium oxide thin film”

- **ISKSR-5**, 5th International Symposium on Kumamoto Synchrotron Radiation, Kumamoto, Japan (Nov 2017) “Valence-selective x-ray fluorescence holography: an example of an yttrium oxide thin film"

- Swedish-Japanese Workshop on Nano-Structure Science by Novel Light Sources, Lund, Sweden (Oct 2017) "Valence-selective X-ray Fluorescence Holography: an example of an Y^{2+}/Y^{3+} thin film"

- **ANC8**, Amorphous and nanostructured Chalcogenides, Sinaia, Romania (Jun 2017) "A combination of anomalous x-ray scattering and x-ray absorption fine structure experiments for the characterization of amorphous GeCu2Te3"

- **ISKSR-4**, 4th International Symposium on Kumamoto Synchrotron Radiation, Kumamoto, Japan (May 2017) “A Combination of AXS and EXAFS with RMC modeling for the characterization of amorphous GeCuTe”

- **JPCOS 2016**, Symposium on Phase Change Oriented Science, Atami, Japan (Nov 2016) "Intermediate-Range Order in GeSbTe Studied by Anomalous X-ray Scattering"

11. A list of paper published during or after the period of the fellowship, and the names of the journals in which they appeared (Please fill in the format below). Attach a copy of each article if available.

Author(s)	Title	Name of Journal	Vol.	Page	Date	Note
S. Hosokawa and J. R. Stellhorn	Development of anomalous x-ray scattering for partial structure studies of random systems	Physics Reports of Kumamoto University	14	53-60	2017	
S. Hosokawa, J. R. Stellhorn, T. Matsushita, N. Happo, K. Kimura, K. Hayashi, Y. Ebisu, T. Ozaki, H. Ikemoto, H. Setoyama, T. Okajima, Y. Yoda, H. Ishii, Y. Liao, M. Kitaura, and M. Sasaki	Impurity positions and lattice distortions in a Mn doped Bi_2Te_3 topological insulator investigated by x-ray fluorescence holography and x-ray absorption fine structure	Phys Rev. B	96	214207	2017	
J. R. Stellhorn, S. Hosokawa, N. Happo, H. Tajiri, T. Matsushita, K. Kaminaga, T. Fukumura, T. Hasegawa, K. Hayashi	A valence-selective X-ray fluorescence holography study of an yttrium oxide thin film	J. Appl. Cryst.	50	1583-1589	2017	
S. Hosokawa, J. R. Stellhorn, H. Ikemoto, K. Mimura, K. Wakita, and N. Mamedov	Lattice Distortions in $TlInSe_2$ Thermoelectric Material Studied by X-Ray Absorption Fine Structure	Phys. Status Solidi A	215	1700416	2018	
S. Hosokawa, K. Kimura, J. R. Stellhorn, K. Yoshida, K. Hagihara, H. Izuno, M. Yamasaki, Y. Kawamura, Y. Mine, K. Takashima, H. Uchiyama, S. Tsutsui, A. Koura, F. Shimojo	Phonon excitations in a single crystal $Mg_{85}Zn_6Y_9$ with a synchronized long-period stacking ordered phase	Acta Materiala	146	273-279	2018	
S. Hosokawa, K. Maruyama, K. Kobayashi, J. R. Stellhorn, B. Paulus, A. Koura, F. Shimojo, T. Tsumuraya, M. Yamasaki, Y. Kawamura, S. Yoshioka, H. Sato	Electronic structures and impurity cluster features in Mg-Zn-Y alloys with a synchronized long-period stacking ordered phase	J. Alloy. Comp.	762	797-805	2018	
B. D. Klee, E. Dornsiepen, J. R. Stellhorn, B. Paulus, S. Hosokawa, S. Dehnen, W.-C. Pilgrim	Structure Determination of a new Molecular White-Light Source	Phys. Stat. Solidi B,		1800083	2018	published online June 8, 2018

S. Hosokawa, J. R Stellhorn, B. Klee, W.-C. Pilgrim, H. Okuda, M. Yamasaki, Y. Kawamura, N. Blanc, N. Boudet	Seeds of $L1_2$ clusters in amorphous $Mg_{85}Zn_6Y_9$ alloy observed via anomalous X-ray scattering	Appl. Phys. Express	11	071402	2018	
J. R. Stellhorn, Y. Ideguchi, S. Hosokawa, N. Happo, T. Matsushita, K. Yubuta, M. Suzuki, H. Ishii, Y. Liao, K. Kimura, K. Hayashi	Temperature dependent local atomic structures in the traditional FeNi Invar alloy by x-ray fluorescence holography	Surf. Interf. Anal.	50	790-794	2018	
J. R. Stellhorn, Y. Ideguchi, K. Kimura, K. Hayashi, N. Happo, M. Suzuki, H. Okazaki, A. Yamashita, Y. Takano, S. Hosokawa	Local Structure of $FeSe_{0.4}Te_{0.6}$ by low-temperature X-ray Fluorescence Holography	Phys. Stat. Solidi B		201800093	2018	Published online July 5, 2018
S. Hosokawa, J. R. Stellhorn, K. Hayashi, T. Matsushita	Applications of a L1-regularized linear regression to x-ray fluorescence holography data of functional materials	Phys. Stat. Solidi B		201800089	2018	published online July 6, 2018
S. Hosokawa, J. R Stellhorn, B. Paulus, K. Maruyama, K. Kobayashi, H. Okuda, M. Yamasaki, Y. Kawamura, H. Sato	The seeds of Zn_6Y_8 $L1_2$-type clusters in amorphous $Mg_{85}Zn_6Y_9$ alloy investigated by photoemission spectroscopy	J. Alloys Comp.	764	431-436	2018	
J. R. Stellhorn, S. Hosokawa, N. Happo, H. Tajiri, T. Matsushita, K. Kaminaga, T. Fukumura, T. Hasegawa, K. Kimura, K. Hayashi	Application of x-ray fluorescence holography to the analysis of interior and surface of an yttrium oxide thin film	Surf. Interface Anal.	1-4	6550	2018	
J. R. Stellhorn, S. Hosokawa, E. Magome	Anomalous X-ray Scattering Experiments for Disordered Materials at the SAGA Light Source	AIP Conf. Proc.			2018	accepted for publication Aug 13, 2018
J. R. Stellhorn, B. Paulus, S. Hosokawa, W.-C. Pilgrim, N. Boudet, N. Blanc, Y. Sutou	A Model for the Fast Phase-Change Mechanism in Cu_2GeTe_3	Phys. Rev. Lett.				Under review

12. Awards during the period of the fellowship (Name of the award, Institution, date etc.)

SRI Poster Award
(Best poster award of the International Conference on Synchrotron Radiation Instrumentation 2018, held in Taipei, Taiwan in June 10-15, 2018)