



Metastable solid solutions of group IV transition metal diborides: An ab initio perspective



C. Gutschka^{1,2*}, L. Zauner², T. Glechner², D. Holec³, H. Riedl^{1,2}

¹ Institute of Materials Science and Technology, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria

² Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria

³ Department of Materials Science, Montanuniversität Leoben, Franz Josef-Straße 18, 8700 Leoben, Austria

* Presenter: christian.gutschka@tuwien.ac.at



full paper

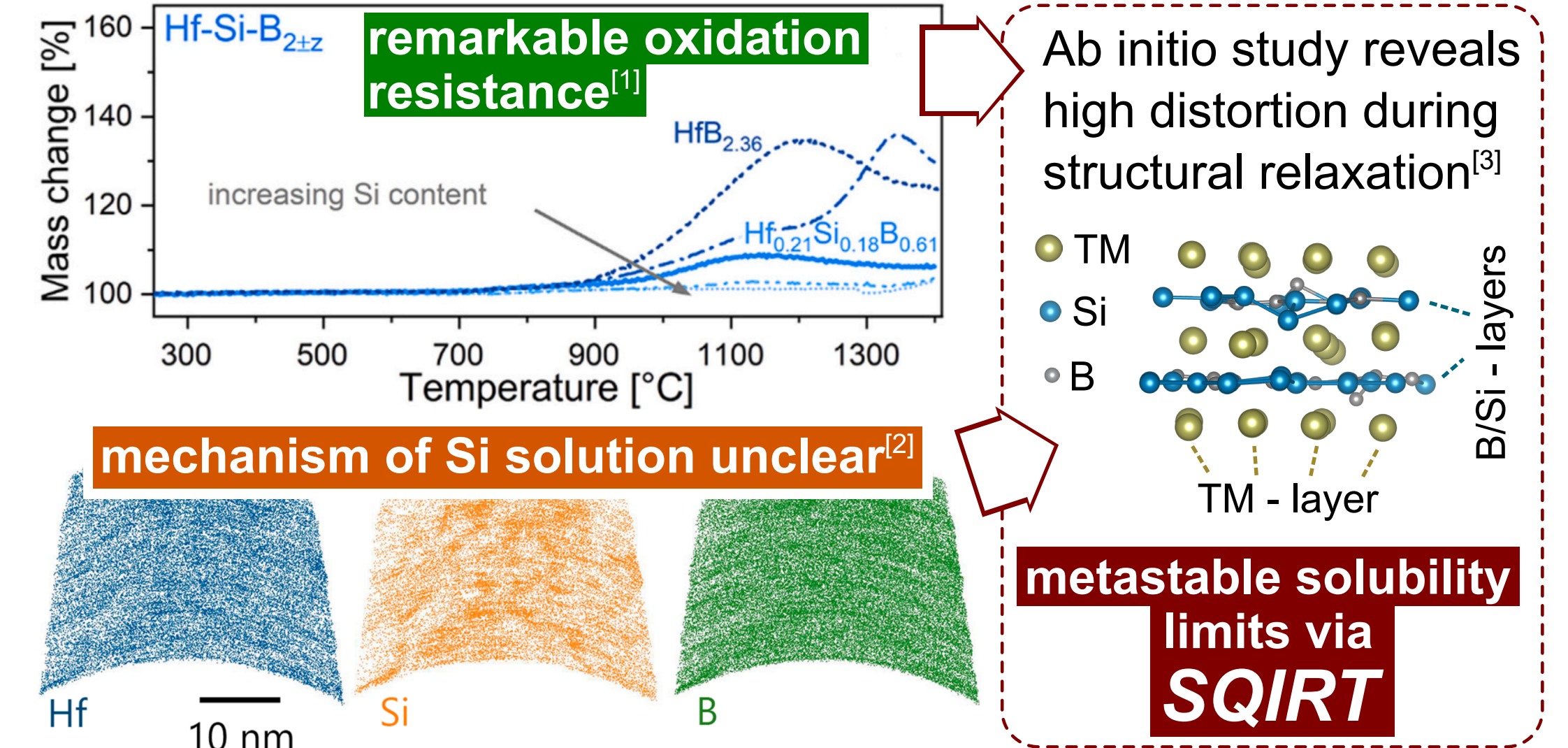
INTRODUCTION

- **Si alloying** significantly **enhances** the **oxidation resistance** of **AlB₂-structured** transition metal **diboride thin films**, synthesized through Physical Vapor Deposition (PVD) [1]
- **X-Ray Diffraction (XRD)** suggests **solid solution** formation, **Atom Probe Tomography (APT)** revealed Si **segregation** and **clustering** [2]
- **Density Functional Theory (DFT)** was applied to **TM-Si-B₂** (TM = Ti, Zr, Hf) systems, assessing their structural and chemical stability, mechanical properties, and bonding character [3]
- The **Special Quasi-random Instance Relaxation Tracking (SQIRT)** method **surpasses equilibrium-based approaches**, yielding Si solubility limits in metastable TM-Si-B₂ compounds

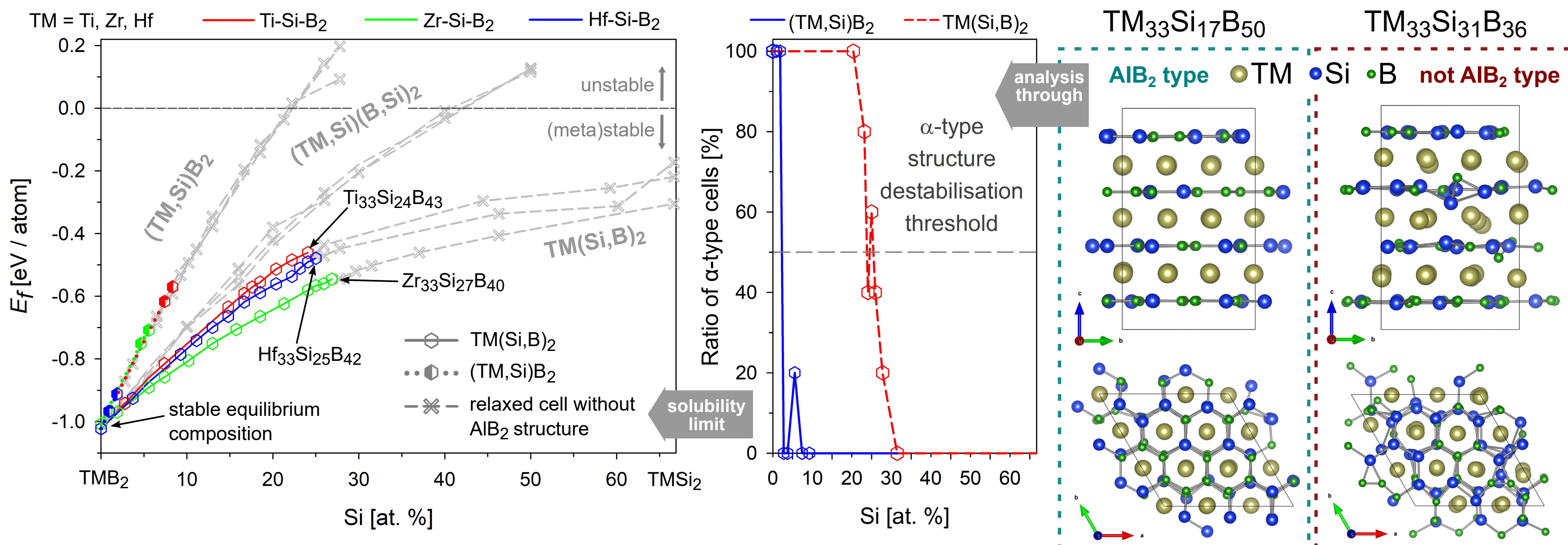
[1] Glechner, Thomas, et al., Surface and Coatings Technology 434 (2022): 128178.

[2] Glechner, Thomas, et al., Corrosion Science 205 (2022): 110413.

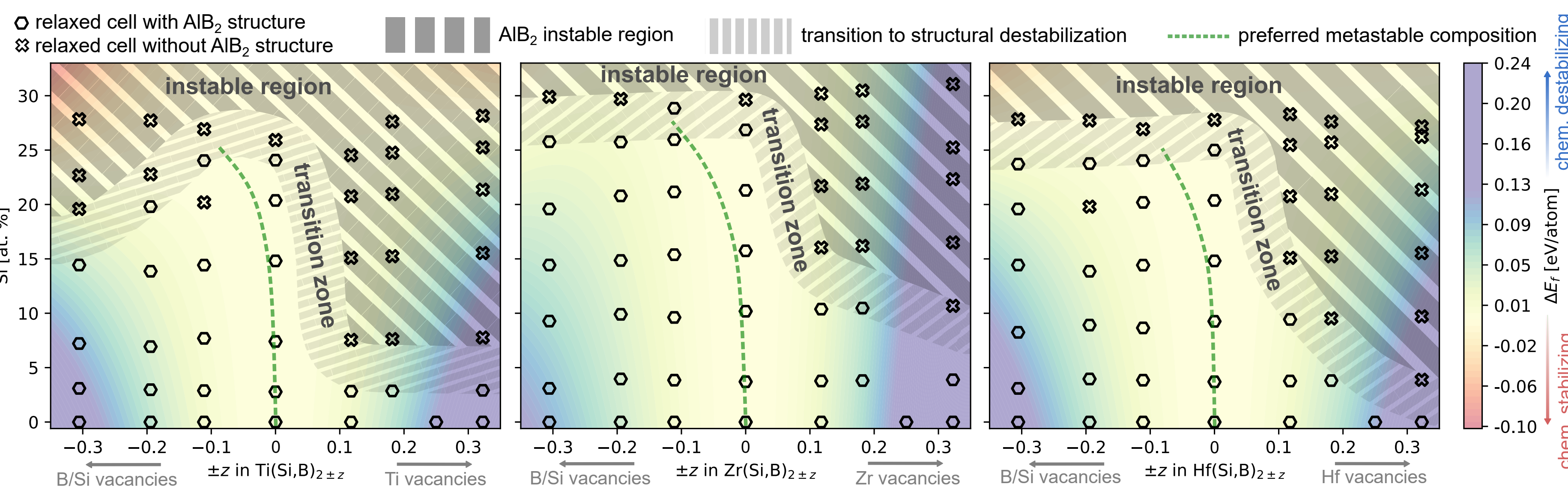
[3] Gutschka, Christian, et al., Acta Materialia 289 (2025): 120857.



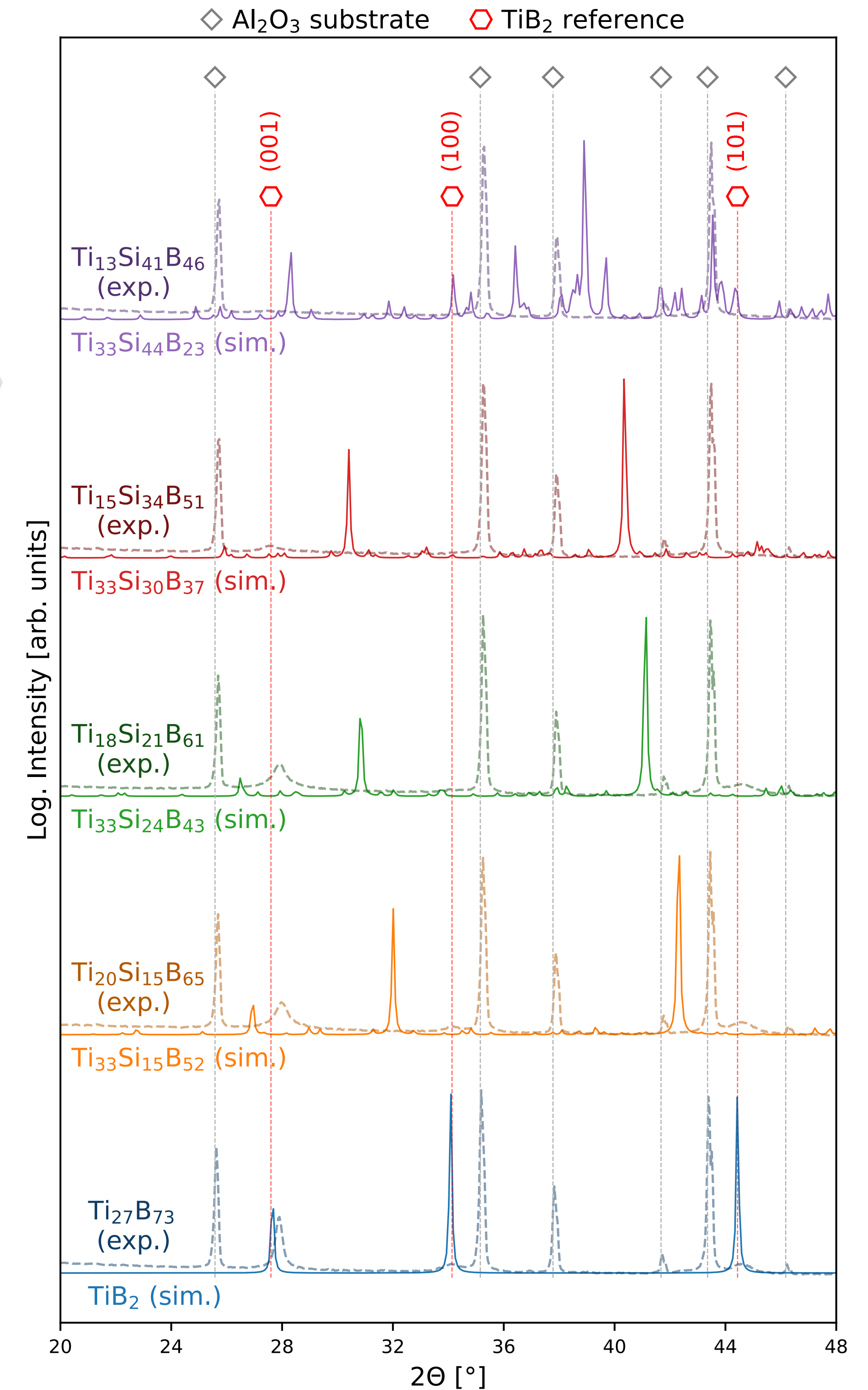
SOLUBILITY LIMITS AND VACANCY EFFECTS



- During structural relaxation, **supercells** with high Si content exhibited **significant distortion**, disrupting AlB₂-type symmetry. This behavior strongly depended on the local chemical environment of Si and B, enabling the SQIRT method to identify metastable solubility limits, beyond which AlB₂-type relaxation sharply declined
- Structural insights combined with sublattice stability, assessed via formation energies (E_f), identify **metastable TM(Si,B)₂ solid solutions** as the most **physically plausible**
- High defect densities in PVD thin films highlight the importance of vacancy-related stability, shown in phase maps including both TM and B vacancies
- **TM vacancies destabilize AlB₂-type structures** across all systems, whereas B vacancies can be accommodated
- At high Si contents, chemical stability shows minimal sensitivity to introduction of B vacancies

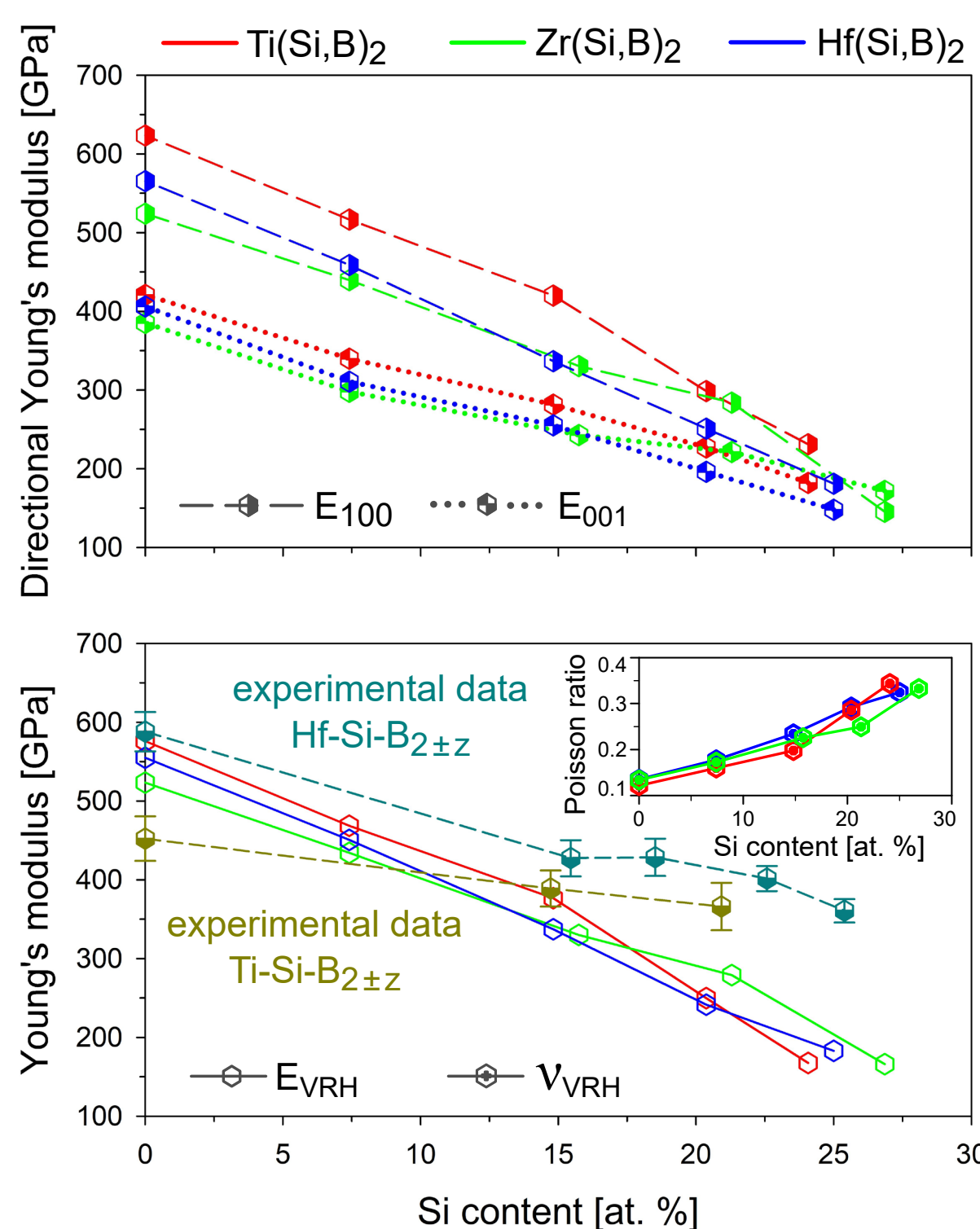


STRUCTURAL INVESTIGATIONS



- Simulated **XRD-patterns exhibit non-indexable peaks** above 24 at. % Si, fitting experimentally observed solubility limits of 21-34 at. % Si in AlB₂ type thin films
- **Matching decrease in 001-peak intensity** of simulation and experiment, w. r. to increasing Si content

MECHANICAL PROPERTIES



- **Decrease** of the directional Young's modulus within basal plane E_{010} , caused by **weak sp^2 - sp^3 bonding between Si and B**
- The c-axis modulus shows substantially lower variation, demonstrating a **reduced elastic anisotropy** with increasing Si content
- **Good match** between **simulated Voigt-Reuss-Hill average** of Young's moduli E_{VRH} and **nanoindentation moduli**, up to 15 at. % Si.
- **Off-stoichiometries** lead to **over-estimation** in indentation modulus of binary **TiB_{2+z}**

CONCLUSION

- First-principles calculations on Ti-, Zr-, and Hf-Si-B₂ systems revealed **metastable Si solubility limits of 24 – 27 at. %** and a strong preference for Si to occupy the B sublattice, yielding the lowest formation energies
- A novel statistical approach using multiple SQS configurations (SQIRT) showed **structural degradation with increasing Si content**, exploring solubility limits independent of near-equilibrium identifiers
- Simulated and experimental XRD patterns confirmed the loss of AlB₂-type symmetry, linked to **Si clustering** and **increased Si-Si bond lengths**
- Metal vacancies destabilized AlB₂-type structures, while B vacancies were sustained without compromising structural stability