Left- or right-handed: Enantiomorph distribution maps for metals and intermetallic compounds

Ulrich Burkhardt[#], Marcus Schmidt, Markus König, Horst Borrmann, Yuri Grin

The assignment of the absolute structure for chiral phases is performed based on electron backscatter diffraction (EBSD) measurements. The Kikuchi pattern evaluation yields spatially resolved enantiomorph distribution maps for polycrystalline materials. These maps were used to cut crystals from enantiopure domains applying focused ion beam (FIB) micro-preparation technique. This allows to verify the EBSD-based absolute structure assignment with that obtained from x-ray diffraction data. The procedure is applied to the chiral compound CoSi (FeSi type) as well as to the β-Mn allotrope and the structurally closely related phase Pt_2Cu_3B. In cases of CoSi and Pt_2Cu_3B, absolute structure assigned from Kikuchi pattern evaluation agrees with the results from x-ray diffraction experiments. Due to differences in diffraction specifics between EBSD and x-ray diffraction, only EBSD provides the assignment of absolute structure for β-Mn.

Interest in chiral phases has increased significantly in recent years, as properties such as unconventional superconductivity, unusual magnetic-order states or enantioselective catalytic properties have been observed. Models for their description show that the absence of an inversion center and other symmetry operations of second kind in the crystal structure are a necessary condition for the occurrence of these properties. The influence of the absolute structure on chirality-dependent properties is often not easy to detect because the co-existence of two enantiomorphs attenuates or even completely cancels the particular effect. Especially for metallic materials, the determination of the absolute structure from single crystal x-ray diffraction (XRD) data is often the only available way to reveal the chirality of a material. Alternatives such as the CBED (convergent beam electron diffraction) method in the TEM (transmission electron microscope) are associated with a considerable preparative effort and hardly allow statements about the distribution of the enantiomorphs on larger scales. Spectroscopic methods frequently used for optically transparent materials to determine non-linear optical properties can only be used to a very limited extent for metallic materials.

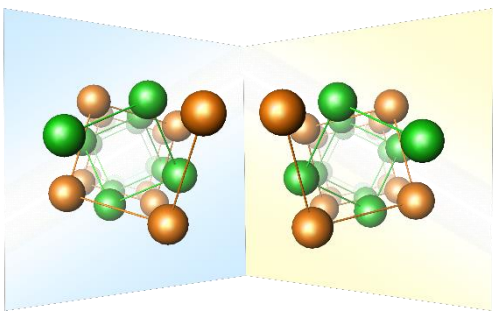

Fig. 1: Equivalent fragments of the crystal structures of β-Mn enantiomorphs. The screw-like arrangements are formed by manganese atoms on different Wyckoff positions (color coded).

Through the further development of EBSD measurement and evaluation techniques, the Kikuchi patterns were shown to be suitable for distinguishing between the two variants of a chiral crystal structure (enantiomorphs). A quantitative comparison of experimental and simulated Kikuchi pattern allows the assignment of absolute structure to the local sample volume examined in the EBSD experiment.

A major motivation for studies on the chiral phase CoSi [1] was to verify whether the XRD method and the EBSD-based absolute structure assignment yield consistent results. These investigations have been performed on high-quality single crystals prepared by chemical vapor transport reaction (https://www1.cpfs.mpg.de:2443/CMS_10). The use of the same specimen for x-ray diffraction and EBSD, respectively, was made possible by applying the focused-ion beam (FIB) micro-preparation technique (https://www1.cpfs.mpg.de:2443/COLL_02). After characterization of CoSi crystals by EBSD in the SEM, cubes of about 40 µm in size were cut out from enantiopure regions. Both methods - XRD and EBSD - gave the same results in the assignment of absolute structure. The adherence to the same (right-handed) coordinate system is important for both the x-ray diffraction experiment and the calculation of the EBSD pattern.

Allotrope β-Mn (Figure 1) is one of the very few chiral element structures. Its remarkable feature is, that the chemically same atoms are located in Wyckoff positions 12*d* and 8*c* (space groups of the enantiomorphs are $P4_132$ and $P4_332$) and have different local environments. In the structurally related

phase Pt_2Cu_3B [2], there is also a chemical difference between the Wyckoff positions 12*d* and 8*c*: copper is located at the 8*c* site; the 12*d* site has a mixed occupation by Pt and Cu in the ratio 2:1. Boron is situated in the voids of the Pt-Cu arrangement. Chemical difference between the 12*d* and 8*c* sites is crucial for x-ray diffraction, since the contribution of anomalous dispersion results in different structure factors of the Bijvoet pairs for Pt_2Cu_3B, but not for β-Mn. Consequently, the absolute structure cannot be determined for β-Mn from x-ray diffraction experiments. However, it can be assigned for both phases by the Kikuchi pattern evaluation technique.

The combination of EBSD, FIB, and XRD was applied to assign absolute structure to the enantiomorphs of β-Mn and Pt_2Cu_3B. The simulated Kikuchi patterns yield comparable absolute structure-dependent differences for β-Mn and Pt_2Cu_3B. For both phases, these differences are sufficiently large to assign the absolute structure by comparison between the experimental and the simulated Kikuchi patterns. By evaluating all Kikuchi patterns from an EBSD measurement, the distribution of the enantiomorphic variants in a polycrystalline sample of β-Mn is obtained (Figure 2). In the case of Pt_2Cu_3B, the absolute structure of the enantiopure domains was confirmed by the XRD analyses of crystals cut from these domains. As expected, the respective β-Mn crystals do not show differences among any Bijvoet pairs, and thus the absolute structure could not be assigned in this way.

The enantiomorph distribution maps open new possibilities to investigate absolute structure-dependent properties for chiral phases - especially when it is difficult to prepare single crystalline samples with defined handedness. In addition, the fractions of enantiomorphs in the complete area investigated can be determined by the presented method (for the surface-near volume part of material which is defined by the beam-penetration depth in the EBSD experiment). The proposed technique is particularly suitable for characterizing thin metallic films enabling the assignment of absolute structure for those materials, which are of technical interest, too.

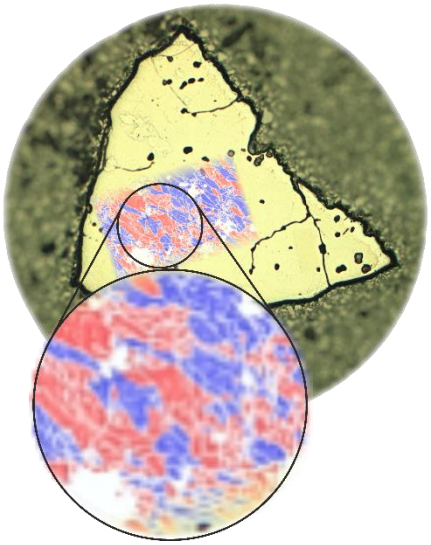

Fig. 2: Enantiomorph distribution map of left (red)- and right-handed (blue) grains of β-Mn in a polycrystalline material. The map is overlaid on an optical bright field micrograph of a metallographically prepared manganese specimen. The grains colored in white belong to the minority phase α-Mn. (small circle: ∅=500 µm)

External Cooperation Partners

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References

[1]* *Absolute Structure from Scanning Electron Microscopy. U. Burkhardt, H. Borrmann, P. Moll, M. Schmidt, Yu. Grin, and A. Winkelmann, Sci Rep.* ***10*** *(2020) 4065, doi.org/10.1038/s41598-020-59854-y*

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[#] Ulrich.Burkhardt@cpfs.mpg.de