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From random stacking faults to polytypes: A 12-layer $NiSn_4$ polytype

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ABSTRACT

$NiSn_4$ grows in diffusion couples (Ni plates with electrodeposited Sn) in a temperature range from room temperature up to 353 K. Previously, the crystal structure of $NiSn_4$ grown at ambient temperature was identified to be an intermediate stacking variant between the orthorhombic $PtSn_4$-type and the tetragonal β-$IrSn_4$-type structure, with a slight tendency towards the tetragonal type (Schimpf et al., Mater. Design 109 (2016) 324–333). Now it is reported that $NiSn_4$ forming at 333 K and above, exhibits a 12-layer polytype (space group $P4_2/nbc$, $a = b = 6.250$ Å, $c = 69.00$ Å) due to ordered incorporation of stacking faults into the structure. This $NiSn_4$ structure was derived by comparison of its diffraction patterns with those of the exhaustively generated $NiSn_4$ polytypes. First-principles calculations on a series of selected $NiSn_4$ polytypes demonstrate that the experimentally observed polytype is energetically favoured as compared to others.

1. Introduction

Irregular stacking in layered crystal structures is a common phenomenon among metals, ceramics and intermetallics. The deviation from the periodic stacking is then called faulting. Sometimes apparent faulting follows itself a specific, e.g., periodic pattern. Well-known examples are the deformation induced transition from fcc to hcp structures [1] with stacking faults on alternate $\{111\}_{fcc}$ lattice planes, the variety of variants of SiC [2], and the more recently emerging long-period stacking order (LPSO) structures in Mg-Zn-rare earth alloys [3,4]. A further type of long-range stacking order due to periodic introduction of faults can also occur in many crystal structures being formed by martensitic transformation [5]. These types of structures can be crystallographically encompassed through the formulation of some kind of superstructure and are called polytypes [6]. The faults are then faults with respect to some original structures, but the periodically faulted structure can be described also by conventional crystallographic means.

$NiSn_4$ is a metastable intermetallic, which forms either during annealing of Ni-Sn diffusion couples at $T = (293 \ldots 373)$ K [7,8] or during solidification of Sn-rich binary Ni-Sn alloys [9,10]. During these processes, $NiSn_4$ develops faster than the thermodynamically stable Ni_3Sn_4 phase. At temperatures above 353 K, $NiSn_4$ appears to decompose into Ni_3Sn_4 and Sn, or does not form at all [8–10].

Previous experimental or theoretical crystal structure studies on $NiSn_4$ favoured the $PtSn_4$ structure and *Aeaa*/*Bbeb*/*Ccce* symmetry (the different symbols represent different choices of the axes; the last one being the standard setting [11])[3] [14,15] or alternatively the $PtPb_4$ structure with $P4/nbm$ symmetry [14]. Both these proposed structure types contain $NiSn_4$ layers as shown in Fig. 1 as fundamental structural unit being stacked in different fashions.

A more detailed X-ray diffraction study complemented by first-principles calculations based on the density functional theory (DFT) [7] has recently confirmed that the crystal structure of $NiSn_4$, forming in electroplated Ni-Sn diffusion couples at ambient temperature, indeed consists of $NiSn_4$ layers as they are characteristic for both the previously proposed $PtSn_4$ and $PtPb_4$ structures (cf. Fig. 1). Occurrence of the $PtPb_4$-type of *layer stacking*, has, however, been rejected on grounds of the observed diffraction patterns. Furthermore, important diffraction features, expected for the $PtSn_4$ type of stacking of the $NiSn_4$ layers, were found to be absent, e.g., the corresponding reflections were smeared out to diffuse diffraction bands. These diffraction patterns have been reconciled with a

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[3] Various works report the *Aba*2 subgroup symmetry [12–14], which misses some symmetry elements present in the $PtSn_4$ structure.

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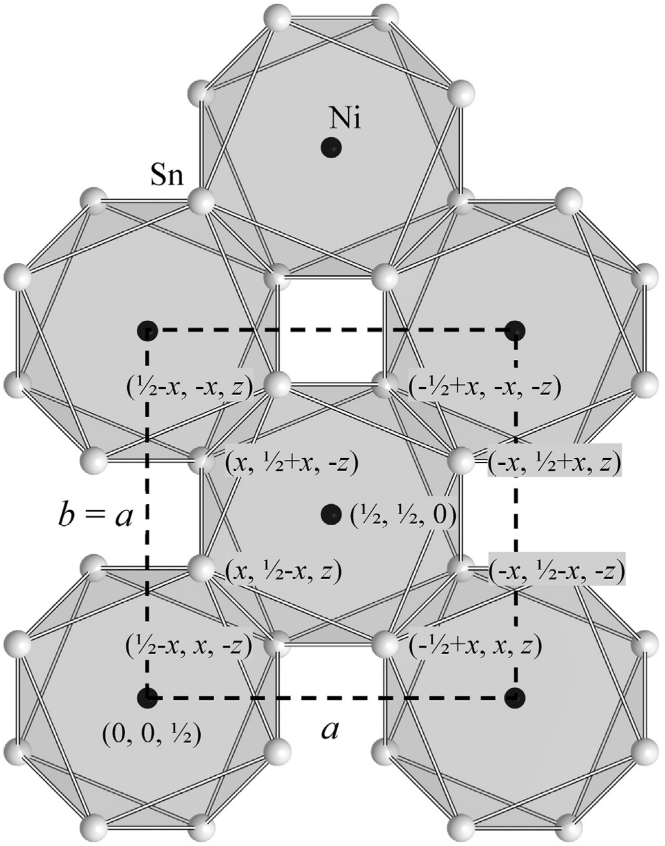

Fig. 1. $NiSn_4$ layer with quadratic *p*4/*nbm* layer-group symmetry [17] as basic constituent of the $NiSn_4$ polytypes with layer-plane lattice parameters $a = b = 6.25$ Å with the layer distance in the stacked structure being $c_0 = 5.75$ Å. The fractional coordinate parameter *x* corresponds to 0.173 and *z* corresponds to ¼. This layer geometry is used in the course of generation of the polytype structures and simulation of their diffraction patterns in the present work. Those geometrical parameters are the same as used previously for simulation of diffraction patterns of stacking disordered $NiSn_4$ [7]. The structure continues infinitely along **a** and **b**.

random stacking of $NiSn_4$ layers intermediate between the periodic stacking reported for $PtSn_4$ (*Aeaa* symmetry) and for a polytype previously described for β-$IrSn_4$ ($I4_1/acd$ symmetry) [16]. That randomness of the stacking leads to pronounced diffuse scattering [7], which is even well visible in powder diffraction patterns. Thereby, the maxima in the diffuse scattering occur at angular positions of (extremely smeared out) reflections expected for the β-$IrSn_4$-type stacking, indicating that the random stacking is closer to that of β-$IrSn_4$ than to that of $PtSn_4$. The disordered structure model, moreover, rejects the idea of a macroscopic break of the tetragonal symmetry in the crystals as it would be expected for the orthorhombic $PtSn_4$ structure.

The present work reports evidence for a long-range ordered stacking variant of $NiSn_4$ with tetragonal symmetry if that intermetallic is grown above ambient temperature. That 12-layer polytype is related to, but still different from the discussed $PtSn_4$ and β-$IrSn_4$ polytypes. DFT calculations reveal that the identified polytype exhibits lower total energy than the other simpler stacking variants, implying thermodynamic control for the formation of the identified polytype.

2. Materials and methods

$NiSn_4$ was generated as intermetallic in Ni-Sn diffusion couples, which were produced by electrodeposition of Sn onto pure nickel plates; for details see Ref. [7]. Thereafter, samples were stored in normal atmosphere at $T = 313$ K, 333 K, 353 K, 373 K for 255 h, while a sample stored at $T = 298$ K for 1440 h [7] serves as reference. After the thermal treatment the residual Sn was etched off by means of o-nitrophenole. Thereby, the intermetallic which has formed upon reactive interdiffusion remains attached at the surface of the nickel plates and can be studied by different analysis methods.

X-ray diffraction (XRD) patterns of the intermetallic on the nickel plates were recorded in Bragg-Brentano symmetrical reflection geometry using a Bruker D8 Advance (Bruker AXS, Karlsruhe, Germany) diffractometer. The diffractometer was equipped with a sealed X-ray tube having Co as anode material. The Co-Kα_1 component from that anode was selected by use of a SiO_2 Johannsson monochromator. Photons were detected using a LynxEye 1D detector. An angular range of $2\theta = 30–80°$ was recorded. In the main text only those ranges of the scans are shown which are needed to arrive at identification of the polytype, applying also the knowledge acquired in Ref. [7]. The complete data are provided as linked Mendeley Data (Leineweber, Andreas; Wolf, C.; Shang, Shun-Li; Becker, Hanka; Liu, Zi-Kui; Schimpf, Christian; Kalanke, P. (2018), “Data for: From random stacking faults to polytypes: A 12-layer NiSn4 polytype”, Mendeley Data, v1 https://doi.org/10.17632/p7cs3xdz24.1).

The polytypes were generated by a dedicated MATLAB® (The MathWorks, Inc., MA, USA) routine (see Sec. 3.2 for details). Diffraction patterns from the polytypes constructed based on the fundamental $NiSn_4$ layer of the geometry depicted in Fig. 1 were simulated using the Vesta program [18]. Identification of symmetry elements and corresponding space groups of the generated polytypes was supported by use of the software FINDSYM [19].

All DFT-based first-principles calculations in the present work were performed by Vienna Ab initio Simulation Package (VASP) [20] with the ion-electron interaction described by the projector augmented wave (PAW) method [21]. The exchange-correlation (X-C) functional of generalized gradient approximation (GGA-PBE) [22] with van der Waals correction (the D3 method [23] adopted herein) was used in the present work, i.e., the PBE + D3 method, by considering the layered nature of $NiSn_4$. Note that auxiliary examinations using other X-C functionals were also performed and similar conclusions were obtained, but they are not shown in the present work, see more details in our previous work [7] to study the stacking disorder of $NiSn_4$. Other details of DFT calculations were reported previously [7], including the selected electronic configurations for each element, cut-off energy, *k*-point meshes (for partial $NiSn_4$ polytypes), convergence criteria of electronic and ionic steps, calculation schemes (relaxations and final static calculations), and fittings of the DFT calculated volume versus energy data points using a four-parameter Birch-Murnaghan equation of state (EOS) [24]. The unreported *k*-point meshes previously [7] for the 4-layer (40 atoms in the supercell), 8-layer (80 atoms), 12-layer (120 atoms), and 16-layer (160 atoms) $NiSn_4$ polytypes were $11 \times 11 \times 2$, $7 \times 7 \times 1$, $7 \times 7 \times 1$, and $5 \times 5 \times 1$, respectively; see Section 3.4 for more structural details.

3. Results & discussion

3.1. Encounter of long-range stacking order in $NiSn_4$

Fig. 2 depicts X-ray diffraction data from the $NiSn_4$-containing intermetallic which has grown on Ni upon interaction with solid Sn at different temperatures. At 313 K, the patterns largely correspond to those of $NiSn_4$ grown at ambient temperature [7]: The 21*l* reflections (and further reflections with $h + k =$ uneven), which are expected to occur at definite positions for e.g. the ideal $PtSn_4$ or β-