Scripta Materialia 194 (2021) 113629

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Diffraction artefacts from twins and stacking faults, and the mirage of hexagonal, polytypes or other superstructures

Cyril Cayron*

Laboratory of ThermoMechanical Metallurgy (LMTM), PX Group Chair, Ecole Polytechnique Fédérale de Lausanne (EPFL), Rue de la Maladière 71b, 2000 Neuchâtel, Switzerland.

ARTICLE INFO

Article history:
Received 9 October 2020
Accepted 9 November 2020

Keywords:
Electron diffraction
transmission electron microscopy
metals and alloys
crystal structure
artefact

ABSTRACT

Recently, a hexagonal phase has been reported in high carbon steels in several studies. Here, we show that the electron microscopy results used in these studies were erroneously interpreted. The extra-spots in the diffraction patterns and the odd contrasts in the high resolution images are not those a superstructure but result from double diffraction and streaking effects due to the presence of twins and stacking faults. We point out a similar unfortunate misunderstanding of these effects in papers reporting the existence of a 9R structure in aluminium or copper, or exotic forms of carbon in diamonds.

In 2015, Liu, Ping *et al.* published a paper entitled "*A new nanoscale metastable iron phase in carbon steels*" claiming for the existence of an hexagonal phase in high carbon steels that they called ω [1]. The authors based their conclusion on the existence of extra-spots in their Selective Area Diffraction (SAED) patterns obtained by Transmission Electron Microscopy (TEM). I immediately wrote a comment on the journal web page (at the bottom of their article [1]) with a link providing the simulations that show that the extra-spots were actually twin artefacts [2]. Despite this warning, Ping *et al.* have continued to (over)publish on the ω-phase [3-9]. Recently, Casillas et al. [10] used dark field imaging and High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) to show that the ω-phase was indeed a twin artefact confirming our conclusion [2]. We fear that our papers will not end the story of the ω-phase mirage in high carbon steels, and we would like to make it clear (again) why this phase does not exist in these alloys. We will also explain our concern about the proliferation of papers reporting exotic superstructures in classical metals and alloys, whereas the conclusions in most of them also come from the illusion given by twin artefacts.

There are two types of artefacts that may be confused with exotic hypothetical polytypes or superstructures. They are detailed in our study [11]. Let us briefly summarized them here:

a) Double diffraction (moiré) effect. This artefact may come from an overlap along the electron beam axis of some domains that are twin-related. It leads to extra-spots created by double diffraction in the SAED patterns, and to moiré fringes in TEM and High Resolution (HR) TEM images. The extra-spots in SAED mimic those of a hypothetical superstructure, such as of the hypothetical ω phase.
b) Streaking effect. This artefact comes from the fact that the diffraction "points" of nanotwins and stacking faults are degenerated into "streaks" because of the very small thickness of the objects. This well-known size effect is at the origin of the peak enlargement in someone X-ray diffractograms. In TEM, it makes that some diffraction streaks of high order Laue zone intercept the Ewald sphere and leave spots in the diffraction plane that can be confused with those of the usual Laue zone of order zero. Here again the spots may mimic those of a superstructure for uninformed microscopists.

In the present work, we have simulated the SAED patterns of paper [1] by assuming a classical bcc structure of Fe, and by taking into account these two possible diffraction effects: (a) the double diffraction between the overlapped $\Sigma3$ twins, and (b) the streak effects along the normal to the $\{211\}_{bcc}$ planes which are the usual habit planes of the nanotwins in bcc structures. We used our computer program GenOVa [12], as we already did in our work on silicon nanowires [11].

Let us start by the SAED pattern of Fig. 1 of Ref. [1] reported in Fig. 1a. The authors stated that it cannot be explained by twins because the "*the incident electron beam is parallel with the twin-*

---

[*] Corresponding author. EPFL, IMX LMTM, Rue de la Maladière, 71b, 2002 Neuchâtel, Switzerland. Phone: 41216954456.

E-mail address: cyril.cayron@epfl.ch

https://doi.org/10.1016/j.scriptamat.2020.11.014

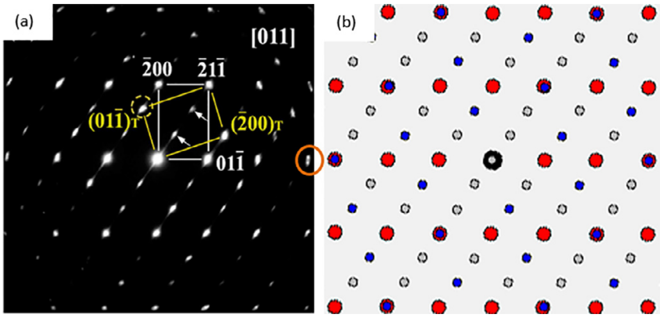

Fig. 1. Simulation of the SAED of Fig. 1 of [1]. (a) Experimental SAED, from [1]. (b) Simulation with GenOVa of (a) with the electron beam along the [011] zone axis, with the spots of the bcc crystal represented by the red disks, those of the twin in blue, and the double diffraction in grey. The orange circle in (a) marks a spitting in two of a diffraction spot.

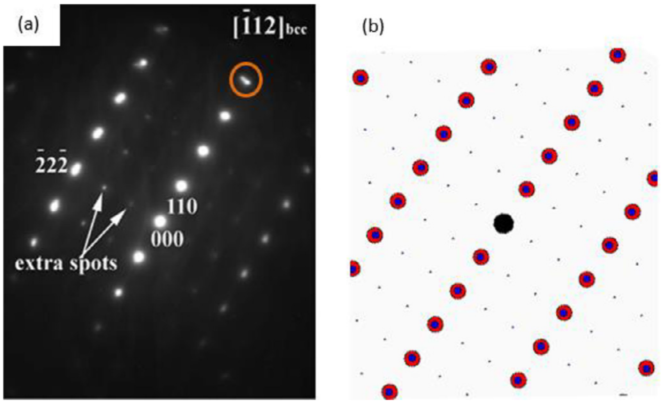

Fig. 2. Simulation of the SAED of Fig. 4 of [1]. (a-c) Experimental SAED, from [1]. (b) Simulation with GenOVa of (a) with the zone axis along [$\bar{1}$12]; the spots of the bcc crystal are represented by the red disks, the spots of the twinned bcc crystal by the blue disks, and the extra-spots coming from a streaking effect of the higher Laue zone along the [112] direction by the black spots. The orange circle marks a spitting in two of a diffraction spot.

ning boundary plane and there is no overlap between the matrix and the twin in the depth direction, it is normally impossible to observe any double diffraction in the twinning diffraction pattern" [1]. It is true that the {$\bar{2}1\bar{1}$} twin plane is oriented along the electron beam which is along the [011] zone axis, and it is probable that the twinned bcc crystals do not overlap, but a dynamical effect is actually possible laterally due to the very small dimensions of the twins. Indeed, double diffraction comes from the deviation of the incident electron beam diffracted by the first crystal, which is then diffracted again by the second twinned crystal. If the second crystal is far from the first crystal, the diffracted beam cannot reach the second crystal, and a double diffraction is impossible; but it is not so for the intricate structure of nanotwins showed by the authors. Indeed, the diffraction angles are of order of 10-20 mrad, and the thickness of the TEM samples are around 100 nm, which means that the diffracted beam is deviated lateraly by 1-2 nm, i.e. the order of magnitude of the size of the nanotwins shown in the TEM image of their Fig. 1a. The argument is also reinforced by the fact that the electron beam is not exactly orientated along the zone axis, which means that the twin plane is slightly tilted. The simulation of Fig. 1a by GenOVa with bcc-Fe and double diffraction is given in Fig. 1b.

The reader can check that the positions of the spots are the same and the change of the intensities are in good agreement with those expected by double diffraction. In addition, by looking more carefully at the experimental SAED of Fig. 1a, one can notice that the diffraction spots are elongated perpendicularly to the {211} twin planes. This is the second artefact, which does not lead here to extra-spots from the higher order Laue zones because the streaks are parallel to the diffraction plane. By looking even more carefully at the spots at high frequencies in Fig. 1a, one can distinguish that they are split in two. This confirms that there are two diffracting bcc crystals, and show that the Σ3 twin relationship is not strictly respected.

Let us continue with the SAED of Fig. 4a of Ref. [1] reported in Fig. 2a. The authors have also rejected the possibility that the extra-spots could come from twins by arguing that "*these extra-spots cannot be treated as double diffraction of the {112}<111>-type twinning structure because the twinning plane is {112}, which is perpendicular to the incident electron beam. In such cases, all matrices and twins will result in exactly the same diffraction spots and the diffraction patterns should be totally overlapped*" [1]. They use this argument several times [4,8]. It is correct, but the authors forget or ignore the streaking effect perpendicularly to the {112} nanotwin planes, although I clearly warned them several times [2]. This effect perfectly explains the extra-spots, as shown by our simulation in Fig. 2b. One can also notice that some spots are split in two, confirming the existence of overlapped twins that are not exactly in Σ3 twin relationship.

Let us end the analysis of Ref. [1] by considering its Fig. 7a reported here in Fig. 3a. As all the SAEDs published by Ping *et al.*, it can be explained by twin effects, as shown by our simulation in Fig. 3b.

Among the numerous papers published by Ping *et al.* over the last five years, no new SAED or HRTEM could be shown that could unambiguously prove the existence of ω-phase. The burden of the proof should not be reversed. Claiming the existence of a new phase should be supported by careful, deep and quantitative studies in which the intensities of the SAED spots and the contrasts of the HRTEM images should be compared with simulations. None of

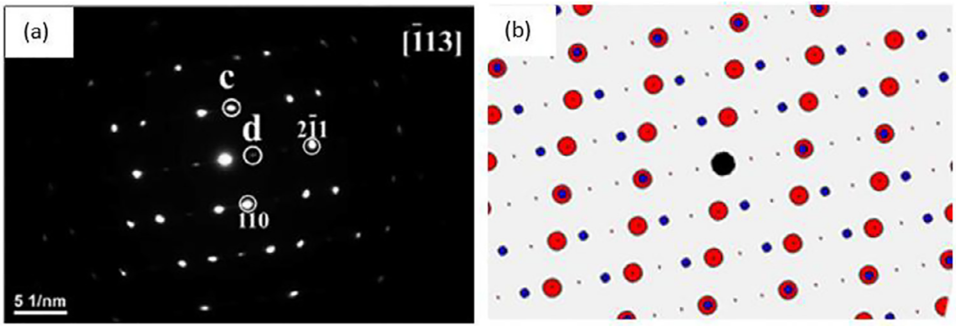

Fig. 3. Simulation of the SAED of Fig.7 of [1]. (a) Experimental SAED. (b) Simulation with GenOVa with two twinned crystals, one oriented along [$\bar{1}$13] (the red disks) and one along [113] (the blue disks). The extra-spots originated by streaks of the higher Laue zones along the [211] direction are given by the black dots.

the papers of Ping's group [1,3-9] responds to the level required for this type of analysis. Actually, all their experimental results can be simulated with the usual bcc structure of iron and classical $\Sigma3$ {112} macro and nanotwins, taking into account double diffraction and streaking perpendicularly to the {112} planes. It is known from decades that in high carbon steels there are 24 variants of martensite in Kurdjumov-Sachs orientation relationship with their parent austenite grain, and that these variants are grouped by $\Sigma3$ twin-related pairs; see for examples [13-16]. It is time to draw a definitive conclusion: there is no ω-phase in high carbon steels, but just twins and stacking faults.

It is not the first time, and unfortunately maybe not the last time, that researchers are confused by diffraction artefacts and think they discovered a "new" hexagonal phase, or more generally a new superstructure. The list of papers would be too long to establish; we will just mention some of them. Some have reported the formation of the ω phase in tantalum after extreme laser deformation [17], but the study suffers the same problems as Ping's ones in steels. The positions and intensities of the spots in the SAED of Fig. 2 of [17] are the same as those of Fig. 3, and they can be equally indexed by double diffraction and streaking effects. Many also claimed for the existence of a 9R phase in pure aluminium and Al alloys, for examples [18-22], but here again, the HRTEM images shown in these works, such as those reproduced in Fig. 4ab, are nothing else than moiré fringes created by overlapped twins. There are also numerous papers claiming the existence of a 9R structure of copper precipitates in iron and steels [23-28], or in copper after irradiation at high temperature [29]; but the only proofs given in these works are here again HRTEM images along <110> zone axes, such as that reproduced in Fig. 4c, that show actually only moiré fringes. The moiré are easily recognized by the fact that the contrasts change all along the interfaces. During the TEM session, the microscopist can also feel the artefact by the impossibility to correctly focalize the image. The illusion of 9R does not stop to metals and alloys. Recently, exotic structures of carbon, such 'M-diamond' ('M' for monoclinic]) and other polytypes such as 2H, 4H, 9R and 15R were reported in papers published in Nature [30,31]. Some stacking faults, and random sequences of stacking faults, may probably be locally assimilated to 2H structures, but the images shown in these studies, such as that reproduced in Fig. 4d, mainly exhibit moiré and odd contrasts that come from of overlapped nanotwins and stacking faults. The misunderstanding of basic diffraction artefacts in recent literature is all the more unfortunate that it was well known by some microscopists in the past. The HRTEM image reproduced in Fig. 4e was obtained in thin

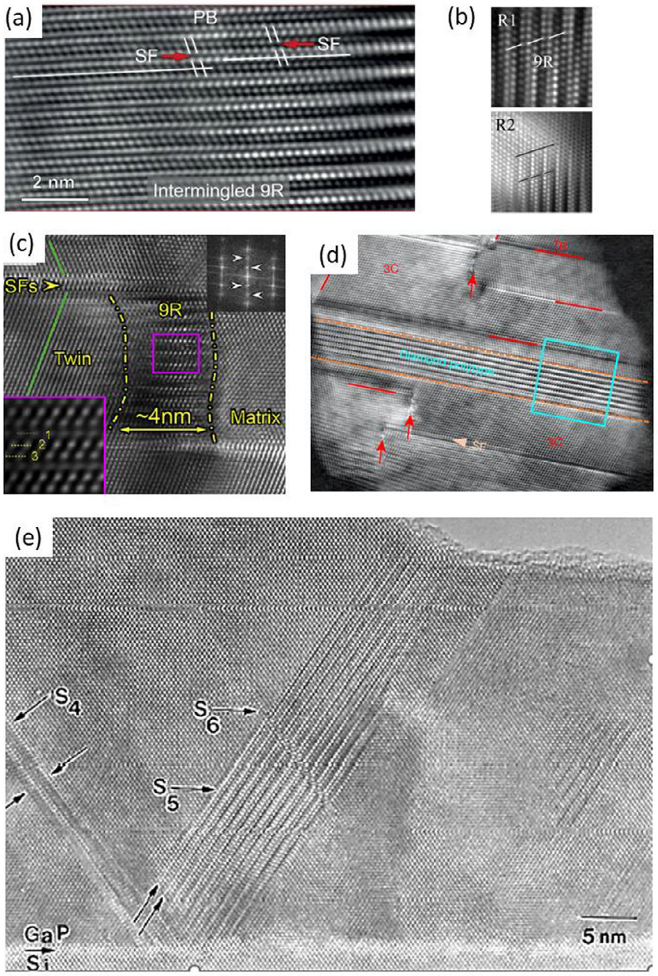

Fig. 4. Moiré fringes in HRTEM or HAADF-STEM images generated by twin overlaps confused with 9R superstructure in (a-d), and correctly identified as an artefact in (e). The images were acquired in (a, b) on aluminium alloys, (c) copper, (d) diamond. The last image (e) is a GaP thin film grown on a silicon wafer. All the images were acquired along a <110> zone axis. Origin: (a) from Fig. 2 of [19], (b) from Fig. 4 of [21], (c) from Fig. 6 of [29], (d) for Fig. 1 of [31], (e) from Fig. 1 of [32].

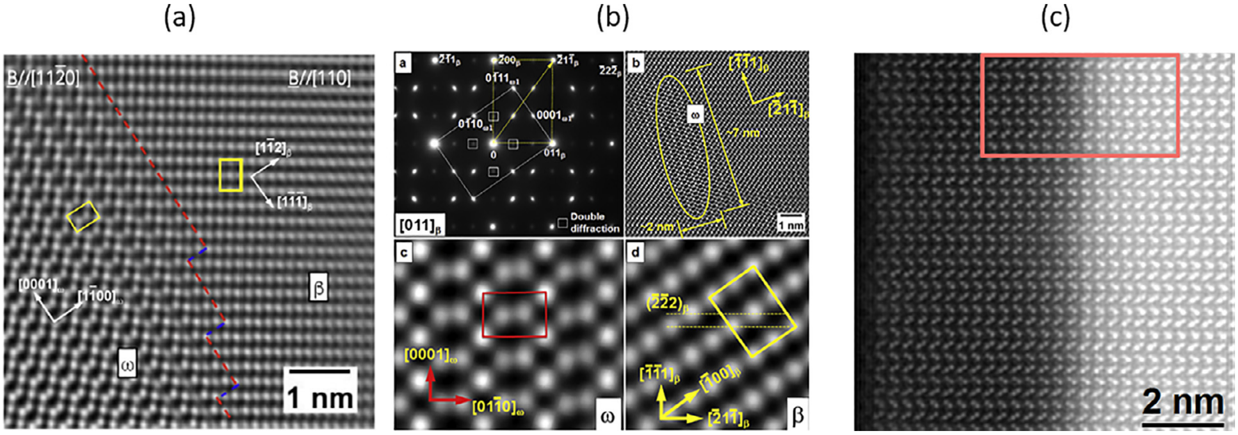

Fig. 5. HAADF-STEM images along the <110> zone axis of real ω phase in Ti alloys (a,b) and of 2H structure in a Si/GaP nanowires. Origin: (a) from Fig. 3 of [40], (b) from Fig. 1 of [41], (c) from Fig. 2 of [42].

films of GaP [32]; it shows the same contrasts as those of Fig. 4a-d, but was naturally considered by their authors as moiré contrasts. Similar images in silicon were also interpreted as moiré [33].

Literature is full of back-and-forth papers between (a) those claiming the existence of new hexagonal or superstructure phases, often published in high rank journals, and (b) the others, less numerous, infirming the conclusions of (a) and warning of the effect of twin artefacts [11,34-39]. It seems that the papers (b) are regularly forgotten, which lets those of type (a) regularly flourish at the same rhythm. We hope that the present paper (of type b) will slow down this unfortunate cycle.

Claiming the existence of new exotic phases from TEM should require a careful study of the SAED intensities and HRTEM contrasts. The HAADF-STEM images should be compared to those expected from the hypothetical structures. Such studies exist. They prove that ω-phase is a real phase in titanium alloys, as illustrated in Fig. 5ab from [40,41] and that a 2H hexagonal form of Si can be obtained on nanowires by an epitaxial method, as shown in Fig. 5c from [42]. The reader can compare these images showing a perfect repeatability of zig-zag motifs made of sharp atomic columns, with those of Fig. 4 with their moiré and blurred contrasts. In Ti alloys, the images of the ω-phase are not always as clear as those of Fig. 5ab because the ω-precipitates are often very small and overlapped by the β matrix (see for example [43,44]), but there is no reason to doubt about the existence of this phase thanks to the studies [40,41], and to many other studies in which the atomic positions and the precise lattice parameters are deduced from X-ray diffraction (see for example [45,46]).

In conclusion, all the SAED and HRTEM shown in literature to infer the existence of a ω-phase in high carbon steels are actually explainable by moiré and streaking effects due to the presence of twins and nanotwins. To our knowledge, the existence of the ω-phase was only proved in titanium alloys. The 9R form of aluminium or copper, or the ‘M-diamond’, 2H, 4H, 9R or 15R exotic forms of carbon were also incorrectly deduced from the same diffraction artefacts.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

References

[1] T. Liu, D. Zhang, Q. Liu, Y. Zheng, Y. Su, X. Zhao, J. Yin, M. Song, D. Ping, Sci, Rep 5 (2015) 15331.
[2] C. Cayron, https://arxiv.org/ftp/arxiv/papers/1511/1511.00591.pdf
[3] D.H. Ping, Acta Metall. Sinica 27 (2014) 1–11.
[4] D.H. Ping, A. Singh, S.Q. Guo, T. Ohmura, M. Ohnuma, T. Abe, H. Onodera, ISIJ International 58 (2018) 159–164.
[5] T.W. Liu, D.H. Ping, T. Ohmura, M. Ohnuma, Electron diffraction analysis of quenched Fe–C martensite, J. Mater. Sci. 53 (2018) 2976–2984.
[6] D.H. Ping, M. Ohnuma, J. Mater. Sci 53 (2018) 5339–5355.
[7] X. Liu, D.H. Ping, H.P. Xiang, X. Lu, J. Shen, J. Appl. Phys. 123 (2018) 205111.
[8] D.H. Ping, H.P. Xiang, J. Appl. Phys. 125 (2019) 045105.
[9] D.H. Ping, S.Q. Guo, M. Imura, M. Ohnuma, X. Lu, T. Abe, H. Onodera, Sci. Rep. 8 (2018) 14264.
[10] G. Casillas, W. Song, A.A. Gazder, Scripta Mater. 186 (2020) 293–297.
[11] C. Cayron, M. Den Hertog, L. Latu-Romain, C. Mouchet, C. Secouard, J.-L. Rouviere, E. Rouviere, J.-P. Simonato, J. Appl. Cryst. 42 (2009) 242–252.
[12] C. Cayron, J. Appl. Cryst 40 (2007) 1179–1182.
[13] H.K.D.H. Bhadeshia, Worked examples in the geometry of crystals, second ed., Institute of Materials, London, 2001.
[14] A. Stormvinter, G. Miyamoto, T. Furuhara, P. Hedström, A. Borgenstam, Acta Mater. 60 (2012) 7265–7274.
[15] A.P. Baur, C. Cayron, R. Logé, Sci. Report. 7 (2017) 40938.
[16] C. Cayron, Mater. Charac. 94 (2014) 93–110.
[17] C.-H. Lu, E.N. Hahn, B.A. Remington, B.R. Maddox, E.M. Bringa, M.A. Meyers, Sci. Rep. 5 (2015) 15064.
[18] S. Xue, Z. Fan, O.B. Lawal, R. Thevamaran, Q. Li, Y. Liu, K.Y. Yu, J. Wang, E.L. Thomas, H. Wang, X. Zhang, Nat. Com. 8 (2017) 1653.
[19] Q. Li, S. Xue, J. Wang, S. Shao, A.H. Kwong, A. Giwa, Z. Fan, Y. Liu, Z. Qi, J. Ding, H. Wang, J.R. Greer, H. Wang, X. Zhang, Adv. Mater 30 (2018) 1704629.
[20] Y.F. Zhang, S. Xue, Q. Li, C. Fan, R. Su, Jie Ding, Han Wang, H. Wang, X. Zhang, Scr. Mater 148 (2018) 5–9.
[21] J.D. Zuo, C. He, M. Cheng, K. Wu, Y.Q. Wang, J.Y. Zhang, G. Liu, J. Sun, Acta Mater. 174 (2019) 279–288.
[22] S.C. Xue, Y.F. Zhang, Q. Li, J. Ding, H. Wang, X. Zhang, Scr. Mater. 192 (2021) 1–6.
[23] P.J. Othen, M.L. Jenkins, G.D.W Smith, W.J. Phythian, Phil. Mag. A 64 (1991) 383–391.
[24] P.J. Othen, M.L. Jenkins, G.D.W Smith, Phil. Mag. A 70 (1994) 1–24.
[25] R. Monzen, M. Iguchi, M.L. Jenkins, Phil. Mag. Lett 80 (2000) 137–148.
[26] H.R. Habibi Bajguirani, Mater. Sci. Engng A338 (2002) 142–159.
[27] G. Han, Z.J. Xie, Z.Y. Li, B. Lei, C.J. Shang, R.D.K. Misra, Mater. Des. 135 (2017) 92–101.
[28] G. Han, C.J. Shang, R.D.K. Misra, Z.J. Xie, Physica B: Cond. Matter 569 (2019) 68–79.
[29] C. Fan, D. Xie, J. Li, Z. Shang, Y. Chen, S. Xue, J. Wang, M. Li, A. El-Azab, H. Wang, X. Zhang, Acta Mater. 167 (2019) 248–256.
[30] Q. Huang, D. Yu, B. Xu, W. Hu, Y. Ma, Y. Wang, Z. Zhao, B. Wen, J. He, Z. Liu, Y. Tian, Nature 510 (2014) 13381.
[31] Y. Yue, Y. Gao, W. Hu, B. Xu, J. Wang, X. Zhang, Q. Zhang, Y. Wang, B. Ge, Z. Yang, Z. Li, P. Ying, X. Liu, D. Yu, B. Wei, Z. Wang, X.-F. Zhou, L. Guo, Y. Tian, Nature 582 (2020) 370–374.
[32] V. Narayanan, S. Mahajan, K.J. Bachmann, V. Woods, N. Dietz, Phil. Mag. A 82 (2003) 685–698.
[33] M. Nerding, L. Oberbeck, T.A. Wagner, R.B. Bergmann, H.P. Strunk, J. Appl. Phys. 93 (2003) 2570.
[34] P.A. Buffat, M. Flüeli, R. Spycher, P. Stadelmann, J.P. Borel, Faraday Discuss. 92 (1991) 173–187.
[35] H. Kohno, N. Ozaki, H. Yoshida, K. Tanaka, S. Takeda, Cryst. Res. Technol. 38 (2003) 1082–1086.
[36] M.I. den Hertog, C. Cayron, P. Gentile, F. Dhalluin, F. Oehler, T. Baron, J.L. Rouviere, Nanotechn. 23 (2011) 025701.
[37] P. Németh, L.A.J. Garvie, T. Aoki, N. Dubrovinskaia, L. Dubrovinsky, P.R. Buseck, Nature Com. 5 (2014), doi:10.1038/ncomms6447.
[38] S.J.B. Kurz, A. Leineweber, E.J. Mittemeijer, J. Appl. Cryst. 48 (2015) 1921–1926.
[39] M. Okugawa, R. Nakamura, A. Hirata, M. Ishimaru, H. Yasuda, H. Numakura, J. Appl. Cryst. 51 (2018) 1467–1473.
[40] Y. Zheng, D. Choudhuri, T. Alam, R.E.A. Williams, R. Banerjee, H.L. Fraser, Scr. Mater. 123 (2016) 81–85.
[41] D. Choudhuri, Y. Zheng, T. Alam, R. Shi, M. Hendrickson, S. Banerjee, Y. Wang, S.G. Srinivasan, H. Fraser, R. Banerjee, Acta Mater. 130 (2017) 215–228.
[42] H. Ikaros, T. Hauge, M.A. Verheijen, S. Conesa-Boj, T. Etzelstorfer, M. Watzinger, D. Kriegner, I. Zardo, C. Fasolato, F. Capitani, P. Postorino, S. Kölling, A. Li, S. Assali, J. Stang, E.P.A.M. Bakker, Nano Lett. 9 (2015) 5855–5860.
[43] M.J. Lai, C.C. Tasan, J. Zhang, B. Grabowski, L.F. Huang, D. Raabe, Acta Mater. 92 (2015) 55–63.
[44] R. Dong, J. Li, J. Fan, H. Kou, B. Tang, Mater. Charact. 132 (2017) 199–204.
[45] R.M. Wood, Acta Metall. 11 (1963) 907–914.
[46] D. Errandonea, Y. Meng, M. Somayazulu, D. Haüsermann, Physica B 355 (2005) 116–125.