Comment on "The two-step nucleation of G-phase in ferrite", the authors: Y. Matsukawa et al. Acta Mater 2016; 116:104–133

Table 1
Crystallographic information used to represent the $Mn_6Ni_{16}Si_7$ G-phase in CrystalMaker™.

Site	Wyckoff coordinate	Fractional coordinates		
		x	y	z
Si I	4b	0.500	0.500	0.500
Si II	24d	0.000	0.250	0.250
Ni I	32f	0.378	0.378	0.378
Ni II	32f	0.178	0.178	0.178
Mn	24e	0.203	0.000	0.000

In the recent publication by Matsukawa et al. [1] a combination of experimental and theoretical techniques were used to investigate the nucleation and growth of $Mn_6Ni_{16}Si_7$ G-phase precipitates in duplex stainless steel. Atom probe tomography and transmission electron microscopy (TEM) were used to observe the number density, size, composition and structure of Mn-Ni-Si clusters after aging for 2000, 5000 and 10,000 h. From their findings, the authors conclude that the precipitation of the G-phase occurs via a two-step mechanism: (1) nucleation and growth as solute clusters and (2) structural transformation into G-phase. This conclusion has a strong scientific basis and is quite plausible given the evidence within this paper and past literature [3,4].

In this comment we aim to rectify the theoretical aspect of the study, in which the simulated TEM selected area electron diffraction (SAED) patterns were generated to make a direct comparison to the experimental patterns. Specifically, the absence of the $(400)_G$ reflection. We believe Matsukawa et al. erroneously attributed this absence, to Fe or Cr occupying the Si lattice site in a 1:1 ratio in the G-phase structure, leading to the conclusion:

"*The simulation of electron diffraction patterns revealed that the extinction of the $(400)_G$ diffraction occurs only when roughly one half of all Si atoms had been replaced with the matrix elements (Fe and Cr) regardless of substitution of Ni and Mn with the matrix elements.*"

In the following paragraphs we attempt to replicate the result obtained by Matsukawa et al. and highlight the unphysical nature of the models they used. We also compare to structures obtained by density functional theory (DFT) calculations, with identical methodology to our previous publication [2], to provide insight into the possible cause of the absence of the $(400)_G$ reflection.

As was done in the original study, the TEM SAED patterns were simulated using SingleCrystal™ within the CrystalMaker® software package. This method uses a standard kinematical theory of diffraction [5]. The input parameters are as follows: Camera length of 100 cm, intensity saturation of 50 and maximum spot diameter of 0.05 1/Å. Further crystallographic information can be found in Table 1 [6]. The SAED simulation theory and conditions were consistent between this work and the work done by Matsukawa et al.

Fig. 1 illustrates the influence of lattice parameter on the $(400)_G$ reflection intensity for three different site occupancies of the Si lattice sites. The variation of reflection intensity with lattice parameter arises due to the relationship between the atomic scattering factor of each element (taken from Ref [7] in CrystalMaker®) to the scattering angle, θ,

of the incident wave with the atom. The scattering angle is related to the d-spacing, d, according to Bragg's Law whereby $d \propto \frac{1}{\sin\theta}$. For changes to the lattice parameter, a uniform change of d-spacings will result, which will therefore change the scattering angle and thus the structure factor according to the equation:

$$F(hkl) = \sum_{n=1}^{N} f_n \, \exp\{2\pi i (hx_n + ky_n + lz_n)\} \qquad (1)$$

where hkl are the Miller indices of the reflection, f_n is the atomic scattering factor of the nth atom in the unit cell and $\{x_n \, y_n \, z_n\}$ are its fractional coordinates. Finally, the square of the magnitude of the structure factor is proportional to the observed intensity.

When using the experimental lattice parameter of the cubic G-phase unit cell ($1.117 \pm 6 \times 10^{-5}$ nm [8]), the results obtained by Matsukawa et al. cannot be replicated. Indeed, the reverse trend is observed

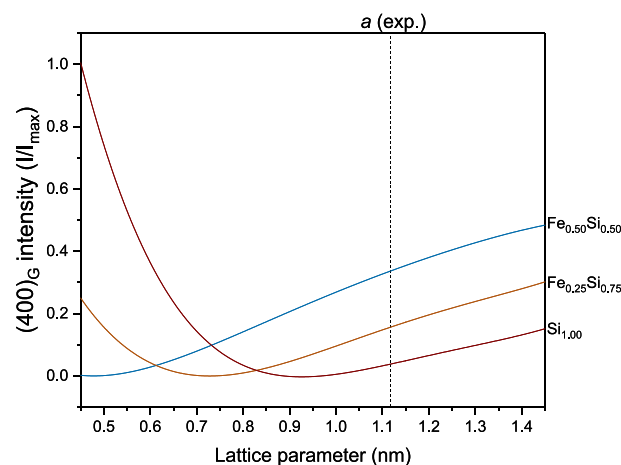**Fig 1.** Relative intensity of $(400)_G$ reflection from the SingleCrystal™ simulated SAED pattern of the ideal $Mn_6Ni_{16}Si_7$ cubic G-phase structure for differing lattice parameters when site occupancy fraction of the 4b and 24d Si lattice sites are $Si_{1.00}$ (red) $Fe_{0.25}Si_{0.75}$ (brown) $Fe_{0.50}Si_{0.50}$ (blue). The lattice parameter as measured by past experiment is represented by the dashed vertical line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
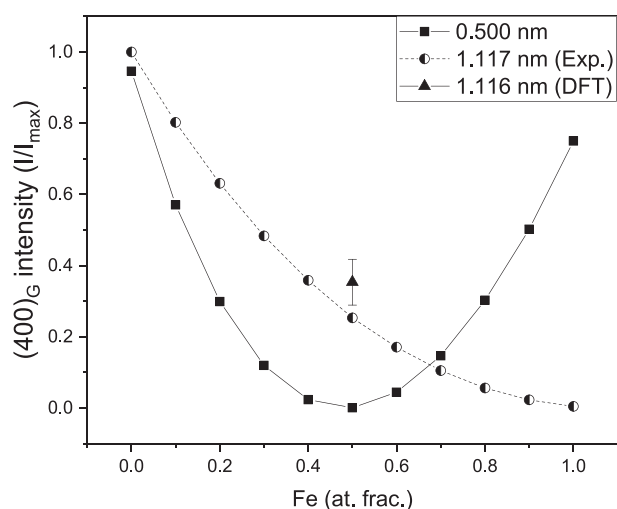
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Fig. 2. Relative intensity of $(400)_G$ reflection from the SingleCrystal™ simulated SAED pattern of the $Mn_6Ni_{16}(Si_{1-x}Fe_x)_7$ G-phase when using a lattice parameter of 0.500 nm (squares) and 1.117 nm (half circles) when x is varied from 0–1. Fully relaxed density functional theory simulations o $Mn_6Ni_{16}(Si_{0.5}Fe_{0.5})_7$ are provided to capture the effect of atomic shuffles (triangle).
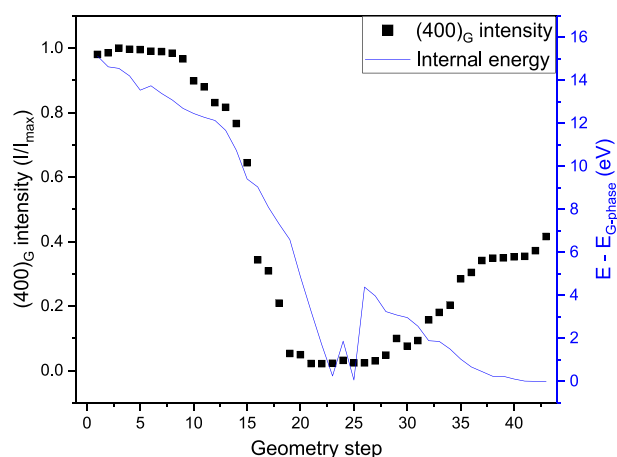

Fig. 3. Relative intensity of $(400)_G$ reflection from the SingleCrystal™ simulated SAED pattern (y_1 axis) of the B2 BCC structure with $Mn_6Ni_{16}(Si_{0.5}Fe_{0.5})_7$ composition as it reconstructs to the G-phase (squares) with the corresponding internal energy (y_2 axis) of each structure (solid line) as calculated by DFT.

between lattice parameters of 0.850–1.450 nm. When using a lattice parameter of ≤0.550 their finding can be reproduced. From a physical perspective, a unit cell of 116 atoms cannot compress to such an extent under laboratory conditions. For comparison, lattice expansion due thermal effects are of the order of 10^{-3} nm in Fe [9] and lattice strain due to the mismatch between the G-phase and the α-Fe matrix is calculated to be 0.017 nm by DFT. Further, the error in distance measurements using electron diffraction [10], and the error between experimental and theoretical SAED patterns [11] are both ~3% (0.034 nm of the experimental lattice parameter of the G-phase). Therefore, a G-phase lattice parameter of ≤0.550 nm is not physically reasonable.

This methodology does not account for atomic shuffles, which are expected to occur with a change in chemistry i.e. substitution of Fe. We therefore simulated 10 cubic unit cells of the $Mn_6Ni_{16}(Si_{0.5}Fe_{0.5})_7$. The theoretical lattice parameter was determined to be $1.116 \pm 4 \times 10^{-4}$ nm. Fig. 2 provides a comparison between the $(400)_G$ intensities, when using a unit cell with a lattice parameter measured by experiment (half circles), unit cell with a lattice parameter of 0.500 nm (squares), and DFT models of $Mn_6Ni_{16}(Fe_{0.5},Si_{0.5})_7$ (triangle). Neither G-phase structures with the experimental lattice parameter nor DFT simulated structures exhibited an absence of the $(400)_G$ reflection in their simulated TEM SAED pattern at 1:1 occupancy ratio of Fe and Si. From these results we believe it is incorrect to conclude that the absence of the $(400)_G$ reflection is due to the 1:1 ratio of Fe on the Si site in the G-phase structure.

The recent publication by our group provides a possible pathway of formation of the G-phase from a BCC packed structure [2]. In the publication by Matsukawa et al. the precipitates without a $(400)_G$ reflection are labelled as "*precursors*" of the G-phase. We hypothesise that the absence of the $(400)_G$ reflection is because the precursor phase is an intermediate structure in-between the BCC packing and G-phase. Fig. 3 shows the variation in $(400)_G$ intensity (black squares) and the associated internal energy (solid line), with reconstruction, when a BCC structure transitions to G-phase with the $Mn_6Ni_{16}(Si_{0.5}Fe_{0.5})_7$ composition. There is a local minimum found at structures 23 and 25 corresponding to the region where there is diminishment of the $(400)_G$ reflection. Fig. 4 displays the simulated SAED pattern of structure 23 and its associated unit cell. This intermediate structure is of P1 symmetry as a small degree of disorder exists in the atomic positions, the unit cell vectors and atomic coordinates are included in the supplementary material. Fig. 5 replicates the analysis done for the G-phase structure where the lattice parameter is varied for three different site occupancies of the Si lattice sites. It is evident that there is still a trend of decreasing $(400)_G$ intensity with occupancy of Fe on the Si site – more significantly – for lattice parameters that are in agreement with experiment and theory.
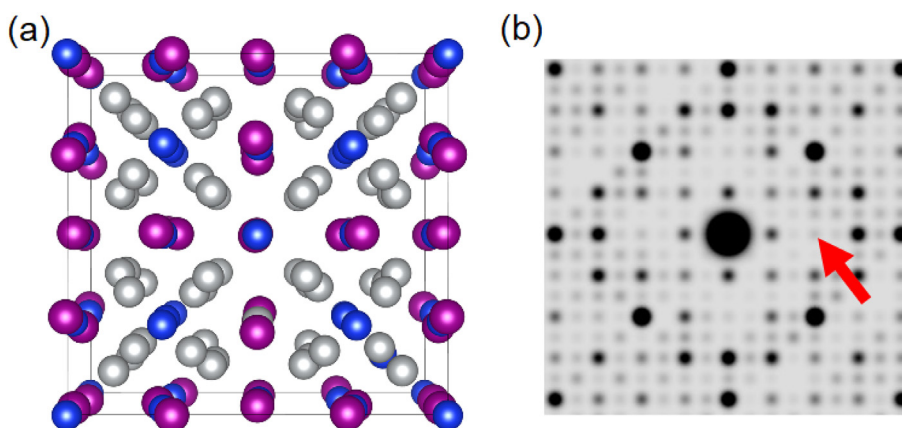

Fig. 4. (a) Intermediate structure from geometry step 23 DFT simulation that corresponds to a local energy minimum in internal energy and (b) the structures corresponding simulated SAED pattern showing the diminished $(400)_G$ reflection (red arrow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
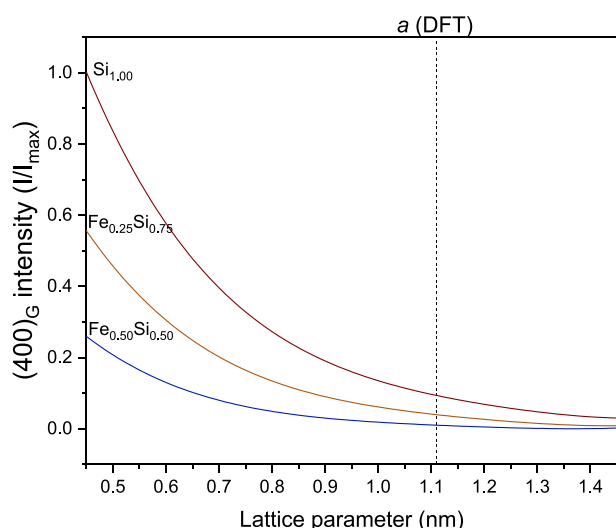
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Fig. 5. Relative intensity of $(400)_G$ reflection from the SingleCrystal™ simulated SAED pattern of the DFT calculated intermediate $Mn_6Ni_{16}Si_{17}$ structure for differing lattice parameters when site occupancy fraction of Si lattice sites are $Si_{1.00}$ (red) $Fe_{0.25}Si_{0.75}$ (brown) $Fe_{0.50}Si_{0.50}$ (blue). The average fully relaxed lattice parameter as calculated by DFT is represented by the dashed vertical line. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In summary, we show that the unphysical lattice parameter of the cubic G-phase $Mn_6Ni_{16}(Si,Fe)_7$ unit cell used by Matsukawa et al. to simulate the TEM SAED patterns leads to a partially incorrect conclusion. When using the experimental lattice parameter or DFT models to attempt to replicate their result, the $(400)_G$ reflection remains for 1:1 Fe:Si occupancies on the Si lattice sites. We provide an alternative explanation using results from our latest publication on the G-phase;

it is possible that the precursor phases exist in an intermediate structure in-between BCC packing and G-phase, which is predicted by DFT. It is still plausible that the occupation of Fe on the Si lattice site contributes to the diminishment of the $(400)_G$ intensity, however, not in a structure that is strictly G-phase.

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3 June 2018
Available online xxxx

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