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Professor C. A. Schuh
Coordinating Editor
Scripta Materialia

Dear Professor Schuh,

<u>Comment for consideration by *Scripta Materialia*</u>

In this comment on the full length manuscript "The two-step nucleation of G-phase in ferrite", by authors: Y. Matsukawa et al. Acta Mater 2016 [1] we seek to correct the theoretical portion of their work on the G-phase. Their publication is a combination of experiment and theory, where the former is sufficient to reach the crux of their conclusion (the two-step nucleation of the G-phase), which we do not dispute.

The contention arises around their simulation of the transmission electron microscopy diffraction pattern that leads to an erroneous conclusion regarding the behaviour of the G-phase. After unsuccessful attempts to replicate their work. We contacted their corresponding author who provided us with one of their example output files [2]. From this we determined that the lattice parameter they used was unphysical and the source of their error.

The implications of this error are significant as the G-phase is ubiquitous to steels and a subject of study in a wide range of technological applications. We provide insight from our latest publication to suggest a possible alternative explanation for the observations by Matsukawa *et al.*

Sincerely,

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References

[1]   Y. Matsukawa, T. Takeuchi, Y. Kakubo, T. Suzudo, H. Watanabe, H. Abe, T. Toyama, Y. Nagai, Acta Mater. 116 (2016) 104–113.
[2]   Y. Matsukawa, Personal communication, (2018).

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

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Abstract. Recently, Matsukawa *et al.* [1] published a paper investigating the nucleation and growth of $Mn_6Ni_{16}Si_7$ G-phase precipitates in duplex stainless steel using experimental and theoretical techniques. The G-phase cubic unit cells simulated by the authors for the theoretical analysis are non-physical, with lattice parameters of 0.500 nm, leading to an erroneous conclusion regarding the site occupancies of Fe in the G-phase. In this comment we use density functional theory results from our previous study of the G-phase [6] to offer an alternative explanation to the experimental observations made by Matsukawa *et al.*, *viz*, the Mn-Ni-Si precipitate is in an intermediate structure resulting from an energy minimum in the process of reconstruction from BCC packing to G-phase.

Keywords: G-phase; Ferrite; Transmission electron microscopy; Density functional theory

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 500, 5000 and 10000 hrs. 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 [2,3].

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 1:1 ratio, 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 their models. Here, structures were obtained by density functional theory (DFT) calculations to provide insight into the possible cause of the absence of the $(400)_G$ reflection.

Although not stated within the study, the TEM SAED patterns were simulated using CrystalDiffract® software with a camera length of 100 cm, intensity saturation of 50 and maximum spot diameter of 0.05 1/Å [4]. When using the experimental lattice parameter of the cubic G-phase unit cell (1.11674(6) nm [5]), the results obtained by Matsukawa *et al.* cannot be replicated. However, when using a lattice parameter of 0.500 nm (as used by Matsukawa *et al.* [4]) their finding is reproduced (see Figure 1). Moreover, upon the substitution of an Fe species, atomic shuffles are expected to occur that is not captured by their method. We therefore simulated 10 cubic unit cells of the $Mn_6Ni_{16}(Si_{0.5},Fe_{0.5})_7$ using DFT following the same methodology as one of our recent publications [6]. The theoretical lattice parameter was determined to be 1.1159(4) nm. Figure 1 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. A G-phase lattice parameter of 0.500 nm is not physically reasonable for a metallic structure at atmospheric pressures. 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.

A recent finding by our group suggests that a transformation from B2 BCC structure to G-phase is a possible route of formation [6]. In the publication by Matsukawa *et al.* the precipitates that do not display a $(400)_G$ reflection are labelled as "precursors" of the G-phase. We hypothesis that the absence of the $(400)_G$ reflection is due the precursor phase existing in an intermediate structure between BCC packing and G-phase. Figure 2 shows the variation in $(400)_G$ intensity (black squares) and the associated internal energy (solid line) with reconstruction when a B2 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. Figure 3 displays the simulated SAED pattern of structure 23 and its associated unit cell.

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 an incorrect conclusion. When using the experimental lattice parameter or DFT models to attempt to replicate their result − the $(400)_G$ reflection remains − when Fe occupies the Si lattice site in a 1:1 ratio. 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 between BCC packing and G-phase, that is predicted by DFT.

References

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[6]   D.J.M. King, P.A. Burr, S.C. Middleburgh, T.M. Whiting, M.G. Burke, M.R. Wenman, J. Nucl. Mater. 505 (2018) 1–6.

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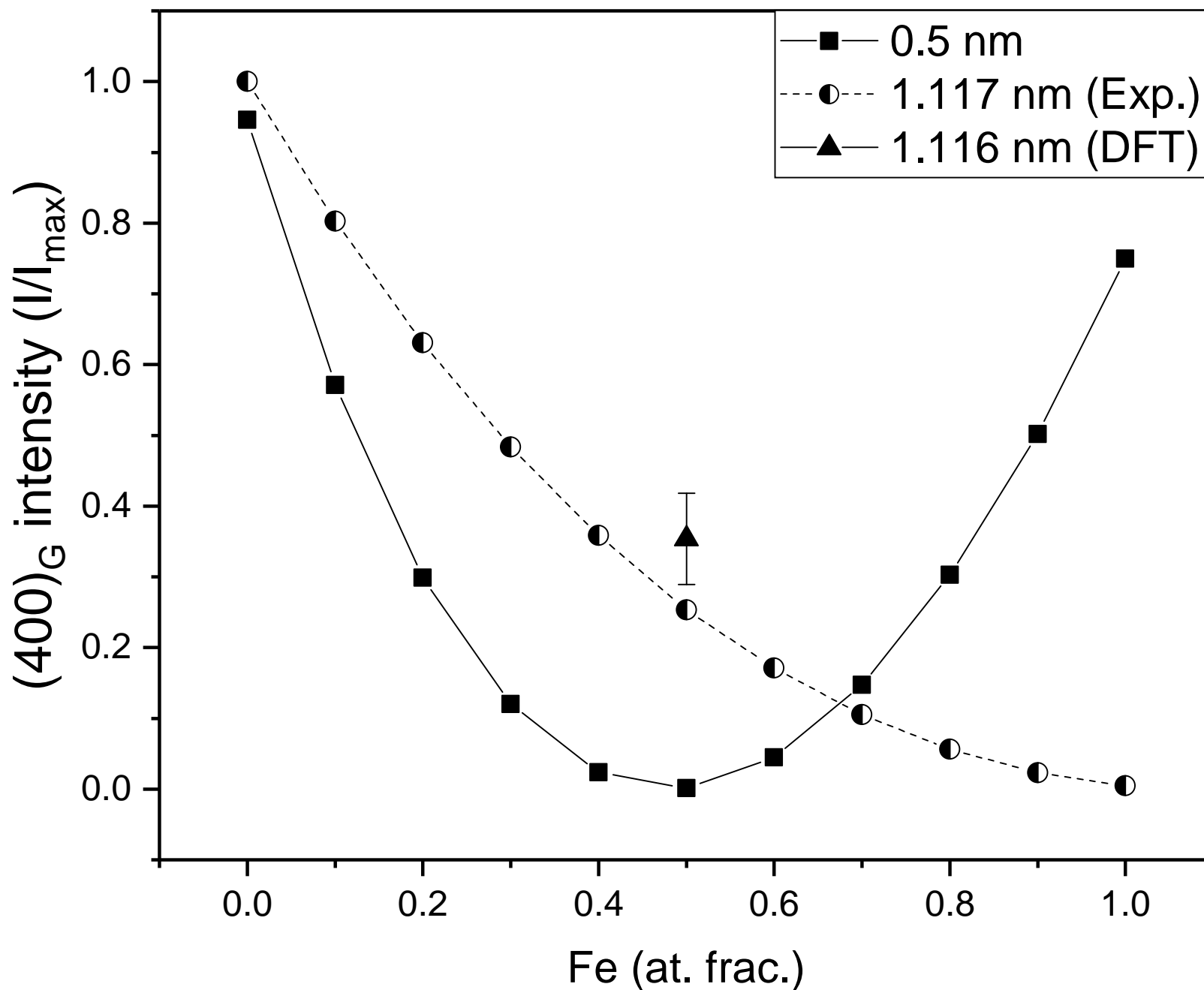**Fig. 1.** Relative intensity of $(400)_G$ reflection from the simulated SAED pattern of the $Mn_6Ni_{16}(Si_{1-x},Fe_x)_7$ G-phase when using a lattice parameter of 0.500 nm (squares) and 1.117 nm (half circles) when x is varied from $0 - 1$. Density functional theory simulations of $Mn_6Ni_{16}(Si_{0.5}Fe_{0.5})_7$ are provided to capture the effect of atomic shuffles (triangle).
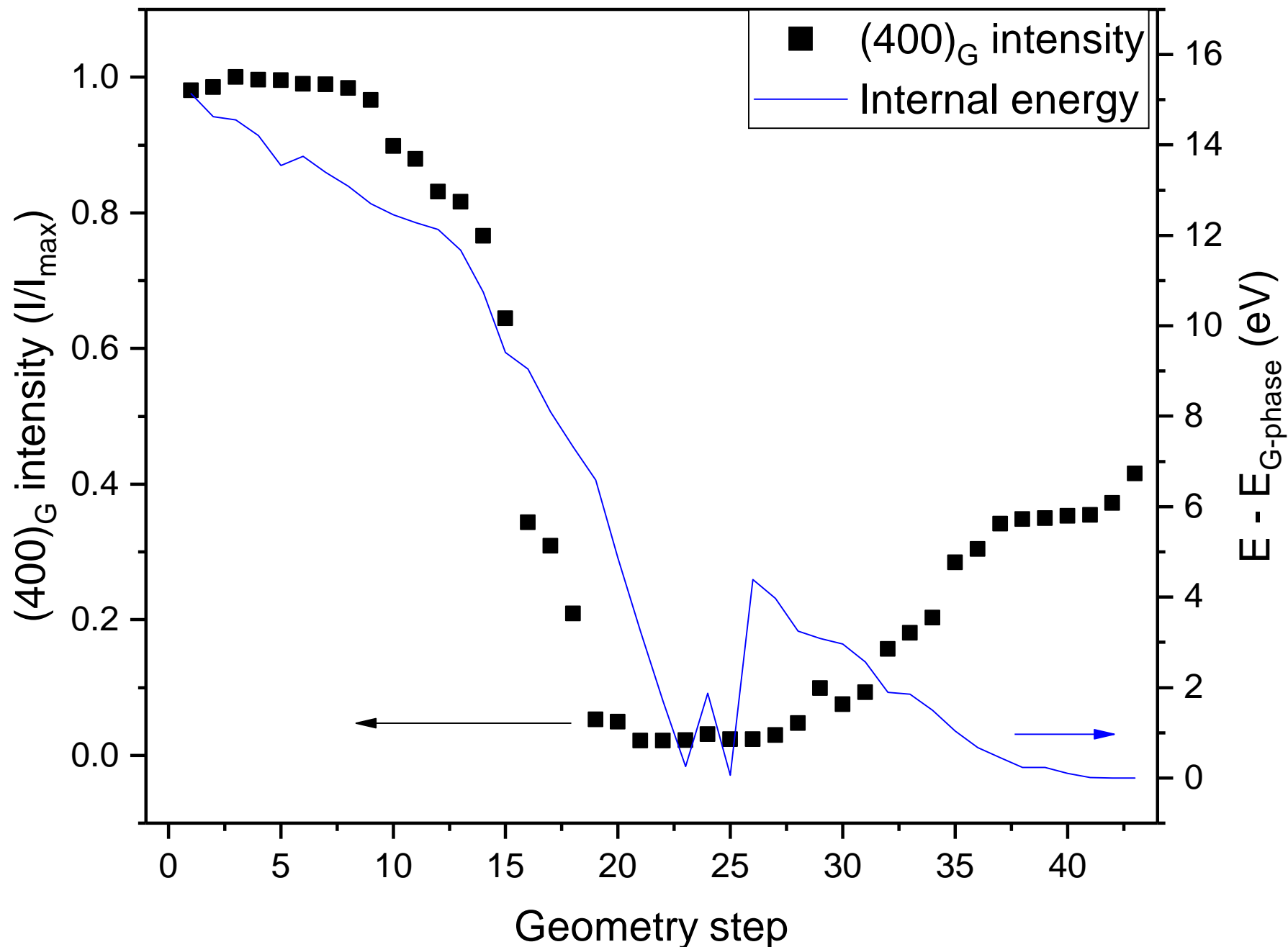
Fig. 2. Relative intensity of $(400)_G$ reflection from the simulated SAED pattern (y_1 axis) of the B2 BCC structure with $Mn_6Ni_{16}(Si_{0.5}Fe_{0.5})_7$ composition as it reconstructs to the G-phase (squares) with the corresponding internal energy (y_2 axis) of each structure (solid line).
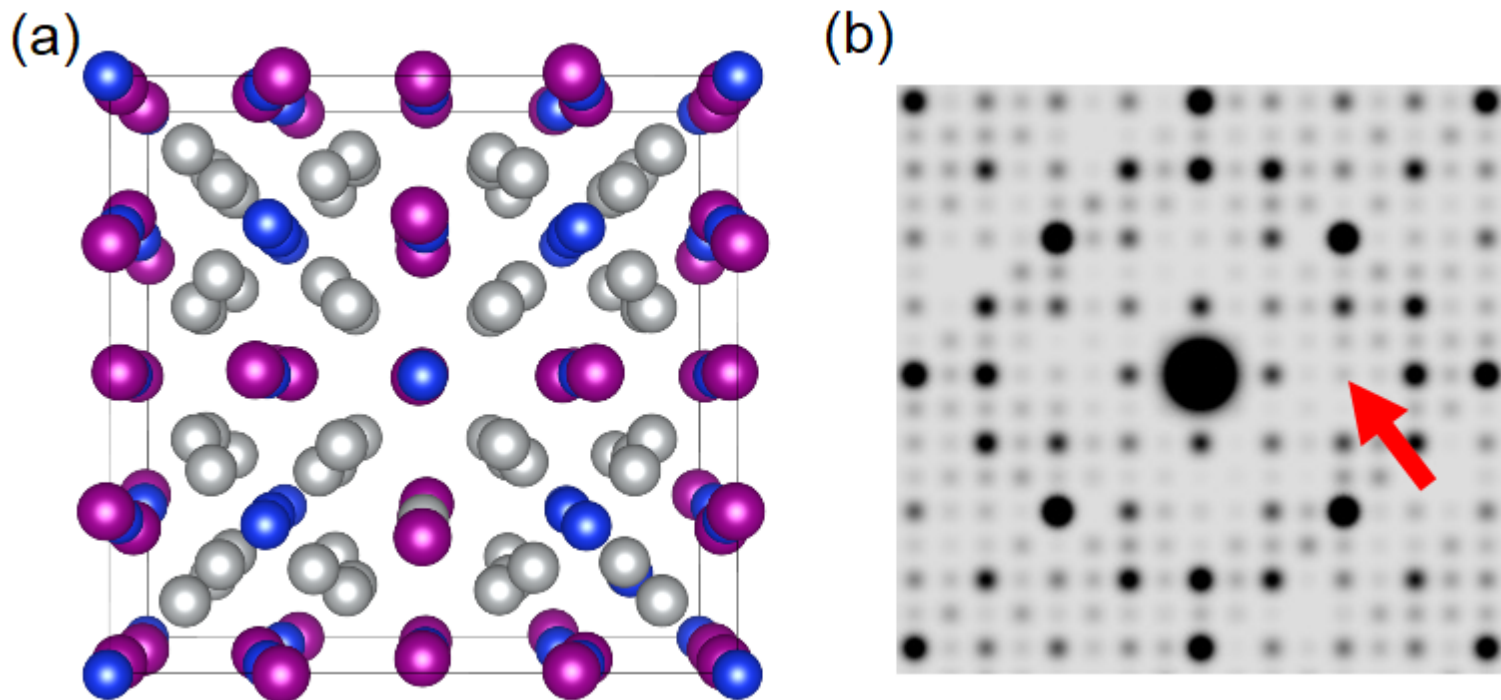
Fig. 3. (a) Intermediate structure from geometry step 23 of DFT simulation that corresponds to a local energy minimum in internal energy and (b) the structures corresponding simulated SAED pattern showing the diminished $(400)_G$ reflection (red arrow).