Full length article

Atomic scale configuration of planar defects in the Nb-rich C14 Laves phase NbFe$_2$

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A R T I C L E   I N F O

Article history:
Received 29 May 2019
Revised 25 September 2019
Accepted 2 November 2019
Available online 8 November 2019

Keywords:
Laves phase
Homogeneity range
Defects
Atomic structure
Scanning transmission electron microscopy
Density functional theory

A B S T R A C T

Laves phases belong to the group of tetrahedrally close-packed intermetallic phases, and their crystal structure can be described by discrete layer arrangements. They often possess extended homogeneity ranges and the general notion is that deviations from stoichiometry are accommodated by anti-site atoms or vacancies. The present work shows that excess Nb atoms in a Nb-rich NbFe$_2$ C14 Laves phase can also be incorporated in various types of planar defects. Aberration-corrected scanning transmission electron microscopy and density functional theory calculations are employed to characterize the atomic configuration of these defects and to establish stability criteria for them. The planar defects can be categorized as extended or confined ones. The extended defects lie parallel to the basal plane of the surrounding C14 Laves phase and are fully coherent. They contain the characteristic $\text{Ti}_2\text{Al}_1$-type (O) units found in the neighboring Nb$_3$Fe$_2$ $\mu$ phase. An analysis of the chemical bonding reveals that the local reduction of the charge transfer is a possible reason for the preference of this atomic arrangement. However, the overall layer stacking deviates from that of the perfect $\mu$ phase. The ab initio calculations establish why these exceptionally layered defects can be more stable configurations than coherent nano-precipitates of the perfect $\mu$ phase. The confined defects are observed with pyramidal and basal habit planes. The pyramidal defect is only ~1 nm thick and resembles the perfect $\mu$ phase. In contrast, the confined basal defect can be regarded as only one single O unit and it appears as if the stacking sequence is disrupted. This configuration is confirmed by ab initio calculations to be metastable.

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1. Introduction

Laves phases are tetrahedrally close-packed (TCP) intermetallic phases composed of small (S) and large (L) atoms with a stoichiometry $LS_2$ and occurring with either a hexagonal (C14) or cubic (C15) structure [1–3]. The crystal structure of TCP phases such as the Laves phases can be described as layered assemblies [1]. The S and L atoms pack as alternating sheets of atoms whose normal is the close packed direction [0001] in C14 or [111] in C15. A stack of four atomic layers with non-uniform spacings forms the fundamental structural unit for all types of Laves phases. A single S layer with atoms ordered in a Kagomé net of triangles and hexagons is followed by an interpenetrating triple layer L-S-L with triangular arrangement of the atoms in each of the three layers. There are two possibilities for placing the triple layer on top of the single S layer, generating two versions of the 4-layered structure unit. These two versions can be placed on the A, B or C lattice sites of the close packed plane in a cubic or hexagonal lattice and the individual versions can be distinguished using a primed (A’, B’ or C’) or unprimed (A, B or C) notation. Using the notation of Frank and Kasper [1], we will designate the two versions of the 4-layer stacks as $\Delta$ (unprimed) and $\nabla$ (primed), respectively. The cubic C15 structure is then generated by stacking these 4-layer units in an ABC sequence similar to a face-centered cubic structure, resulting in a 12-layer unit cell (and denoted as $\Delta\Delta\Delta\Delta$). An alternating $\text{AB}^\prime$ sequence ($\Delta\nabla$) produces the hexagonal C14 structure, the unit cell of which then is composed of eight layers of atoms whose normal is [0001]. Schematic illustrations of the C14 unit cell and the atomic stacking of the S and L layers...
are presented in Figs. 1a and b, respectively. These illustrations are representative of the stoichiometric composition, LS2.

Laves phases are not necessarily restricted to stoichiometric compositions and sometimes in binary systems but often in ternary systems, they can exist over a wide range of compositions. In the binary cases, the spread in off-stoichiometric compositions can be observed both on the S-rich side and on the L-rich side [4–6]. A well-studied example is the C14 Laves phase NbFe2, which is reported to exist between 25.1 and 37.6 at. % Nb [7]. So, a rather interesting fundamental question arises: How are deviations from stoichiometry accommodated on the Fe-rich side and on the Nb-rich side? One immediate explanation is that excess atoms can be accommodated by anti-site defects. Indeed, several X-ray diffraction studies have shown that the lattice parameters continuously change on both sides of the 1:2 stoichiometry indicating the existence of anti-site atoms [8–12]. Since we have large and small atoms, it is easier to envision accommodation of excess atoms through anti-site defects on the Fe-rich side of NbFe2. However, due to strain and charge transfer considerations (see below) it is not immediately clear that such accommodation alone is adequate to account for deviation from stoichiometry on the Nb-rich side. Presumably, the strain energy can be relaxed at high temperatures, and then larger stoichiometric ranges will be available. This is evidenced in the Fe-Nb system from recent phase diagram evaluations where it is confirmed that although an Fe-35 at. % Nb alloy is at the limit of the C14 single phase regime at room temperature, the stability range extends to a maximum of ~37.5 at. % Nb at higher temperatures [7]. Thus, a binary Fe-Nb alloy with an overall composition between 35 at. % Nb and 37.5 at. % Nb will be a single-phase Nb-rich C14 Laves phase at high temperature. However, upon cooling from elevated temperatures, it can be anticipated that the Nb-rich μ phase (Nb6Fe) will precipitate as dictated by the phase diagram [7].

The μ phase has a rhombohedral crystal structure (R3m, W6Fe2 prototype); see for example, [1,2,13]. According to a classification of TCP crystal structures by Shoemaker and Shoemaker [14], both Laves and μ phases belong to the same group of TCP phases characterized by juxtaposed pentagonal antiprisms. This correlation is reflected in the trends of structural stability with the number of valence electrons that is similar for the Laves and μ phases [15,16]. The unit cell for the μ phase is presented in Fig. 1c along with the atomic stacking sequence perpendicular to the basal plane in Fig. 1d. In principle, the μ phase stacking is composed of two very different 4-layer units; one is identical to the S-[L-S-L]-type arrangement (∆) of the S and L atoms found in the Laves phase and shown in Fig. 1b, while the other is made of one single layer

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Fig. 1. Comparison of the crystal structures of (a,b) NbFe2 C14 Laves phase and (c,d) Nb6Fe2 μ phase. The characteristic 4-layer-stacks of both structures are marked following the nomenclature of Frank and Kasper [1].
of S and a three-layer stack of L-L-L, which is the characteristic atomic arrangement of Zr₃Al₇-type structures [17,18] and denoted by O. Stacking the resulting combined Laves and Zr₃Al₇-type 8-layer units (ΔO) in a sequence ABC just as in a fcc structure generates the μ phase crystal structure with 24 layers of atoms in the unit cell as shown in Fig. 1d.

Thus, there is a fair level of correlation in atomic stacking between the Laves and the μ phase and intergrowth of the structural units can be envisioned. Indeed, planar defects with a C14-type structure were found in the μ phase Mo₃Fe [19] and Nb₃(Cr,Ni)₂ [20]. Ye et al. [21] electrolytically extracted C14 Laves phase crystals from a ferritic superalloy and, using high-resolution electron microscopy, found various planar defects including ΔO slabs of the μ phase on the (0001), (1–100) and (1–10–1) planes of the Laves phase. When comparing the atomic distances and symmetry on different planes of the C14 Laves phase and the μ phase in the Fe-Nb system, the atomic arrangements on the (10–11) planes of both phases (in hexagonal indexing) differ insignificantly from each other [22]. However, a locally confined precipitation of μ phase or polytypes of it that contain ΔO slabs within a C14 matrix (∆V slabs) can result in elastic strain energy, due to the higher density of layers in the L-L-L stack as compared to the L-S-L stack. This would have consequences on the relative structural stability of such atomic configurations.

In this study, single-phase stoichiometric and Nb-rich NbFe₂ Laves phase specimens were slowly cooled to room temperature and transmission electron microscopy (TEM) was performed to characterize the defect structures. Special attention is devoted to characterizing the faults in the Nb-rich Laves phase by high resolution scanning transmission electron microscopy (HRSTEM). The aim is to elucidate the role of the excess Nb atoms on local atomic arrangements at planar defects. The HRSTEM observations are complemented by density functional theory (DFT) calculations on the energetics and stability as well as by analysis of chemical bonding in different atomic configurations associated with these planar defects.

2. Experimental procedure and calculation methods

2.1. Material synthesis and experimental methods

Single-phase alloys of the compositions Fe-33.0 at.% Nb and Fe-35.0 at.% Nb were produced in the form of cylindrical ingots of ~350 g, in diameter and ~100 mm in length, by levitation melting in a cold crucible device. The starting materials were Fe of 99.95 wt.% purity and Nb of 99.9 wt.% purity. The alloys were then drop-cast into an alumina crucible that was preheated to 1200 °C. The temperature was held for 45 min and then the crucible was cooled down at a rate of 5 K/min to ambient temperature. For the off-stoichiometric alloy, an additional homogenization heat treatment was performed in a high-purity Ar inert gas atmosphere at 1350 °C for 50 h followed by slow cooling (5 K/min) to room temperature. A more detailed description of the alloy synthesis is given in [23]. Chemical analysis of the final alloys revealed impurity levels of ~300 wt. ppm O, ~50 wt. ppm C, and < 10 wt. ppm N.

The single-phase microstructure of the resulting alloys was verified by scanning electron microscopy (SEM) using a JEOL JSM-6490 microscope and by X-ray diffraction (XRD) employing a GE Seifert XRD 3003 diffractometer with Co-Kα₁ radiation. Electron probe microanalysis (EPMA) was performed using a JEOL JXA-8100 instrument to measure the phase composition and characterize the chemical homogeneity of the samples.

Microstructure was studied in detail by TEM. Conventional TEM, particularly by bright field (BF), dark field (DF) and weak beam dark field imaging (WBDF), was performed in a FEI Phillips CM20 microscope operated at 200 kV. Scanning TEM (STEM) coupled with energy dispersive X-ray spectroscopy (EDS) were conducted in an FEI Titan Themis 60–300 microscope with an acceleration voltage of 300 kV. For STEM imaging and STEM-EDS probe, semi-convergence angles of 23.8 and 17 mrad with probe currents of 50–80 pA were used, respectively. For realizing high angle annular dark field (HAADF) conditions the inner and outer semi-collection angles of the annular detector were set to 73 and 200 mrad. Under low angle annular dark field (LAADF) conditions the inner collection angle was reduced to 20 mrad (for 17 mrad convergence angle) and 26 mrad (for 23.8 mrad convergence angle) by simply increasing the camera length. STEM-EDS data was acquired with a “Super-X” system of four synchronized detectors with a nominal detector area of 120 mm² and maximum total solid angle of 0.7 sr. Samples with 3 mm in diameter and 500 μm in thickness were obtained by electrical discharge machining. After mechanical polishing to 150 μm thickness, the foils were twin-jet polished to perforation using a Struers Tenupol-5 and an electrolyte of 90 vol.% ethanol and 10 vol.% perchloric acid at ~30 °C.

2.2. Calculation methods

First-principles calculations of the structure and energetics of defects were performed within the framework of DFT using plane-wave basis sets as implemented in the Vienna ab initio simulation package (VASP) [24–26] and the Perdew-Burke-Ernzerhof (PBE) [27] exchange-correlation functional in the generalized gradient approximation (GGA). The projector augmented wave (PAW) method [28] was used to treat the ion-electron interactions, and the k-point meshes were created using the Γ-centered Monkhorst-Pack scheme [29].

Convergence tests ensured that a Brillouin zone integration using grids with a k-point spacing of approximately 0.13 Å⁻¹ (∼12,000 k-point×atom) as well as a plane-wave cut-off energy of 350 eV is sufficient for high accuracy, i.e., for energy differences <1 meV/atom (~0.1 kJ/mol). All bulk structures were fully relaxed with respect to cell size, shape, and internal coordinates. For surface calculations the stacking fault structures are constructed using fully relaxed C14 with O unit obtained from μ phase which itself is relaxed at C14 basal lattice parameters.

The DFT energies of the atomic structures are obtained for a magnetically ordered (ferrimagnetic) or a nonmagnetic state. This is an approximation, since NbFe₂ shows paramagnetic disorder at room temperature. It cannot be employed for the basal synchroshear-formed stacking fault (BSSF) in stoichiometric NbFe₂, since its formation energy is negative in the ferrimagnetic state, but positive in the paramagnetic state. A paramagnetic calculation becomes possible in this exceptional case, if we first determine the energy difference ΔE between the C15 and C14 Laves phases and then employ a revised version of the method of Chu et al. [30], noting that the BSSF consists of two simple stacking faults

\[ \gamma_{\text{BSSF}} = 2 \times \gamma_{\text{SF}} = 2 \times \frac{12\Delta E}{\sqrt{2}a_{\text{C14}}} \]

For the C14 Laves phase in NbFe₂, the paramagnetic energy difference is ΔE = 12.6 meV/atom [31], the paramagnetic lattice parameter is a₄₄ = 0.477 nm, and therefore the energy of the BSSF is \( \gamma_{\text{BSSF}} = 123 \text{ mJ/m}² \). Nevertheless, the reference energy for the bulk C14 and μ phases are consistently taken for the ferrimagnetic state in the stability analysis in Section 3.2 with spin alignments down-up-down (Fe₅a Fe₆b Nb₄f) and up-up-down-down (Fe₁₈b Fe₁₃b Nb₁₂b Nb₁₂c).

Analysis of chemical bonding was carried out by employing an all-electron, full-potential method with atom-centered numerical orbitals as implemented in the FPLO code (version 9.01) [32] with the PBE [27] and Perdew-Wang [33] parametrization for the exchange-correlation effects. A scalar relativistic Hamiltonian was applied to the semi-core and valence electrons, while the core
electrons were treated in a fully-relativistic way. Literature crystal-
tal structure information for NbFe$_2$ and Nb$_5$Fe$_7$ [34] was used for
the calculation of the bulk electronic structure. Because both crys-
tal structures were not refined using the X-ray diffraction data,
the full structural optimization of the initial models was carried out
using the GGA with a force criterion of 5 meV Å$^{-1}$. The optimized
structures were used for further analysis of chemical bonding.
The latter is based on the electron localizability approach combining
electron density (ED) and electron localizability indicator (ELI) [35].
The electron density is analyzed within the quantum theory of
atoms in molecules (QTAIM) [36]. ELI [37] was calculated in the
ELI-D representation [38,39] by a module implemented in the FPLO
code [40]. Topological analysis of the ED and the ELI-D was carried
out by the program DGrid [41].

3. Results

3.1. Experimental results

An examination of the two slowly cooled specimens by SEM
and XRD revealed that the microstructure in both instances was
composed of single-phase C14 NbFe$_2$ grains with diameters in the
range of 50 to 200μm (Fig. 2). EPMA measurements confirmed a
chemically homogeneous microstructure with no evidence for ei-
ther micro- or macro-segregation. Some fine precipitates with di-
ameters $<$ 1μm were found on the grain boundaries and could be
identified as oxides and carbides of the NbO and (Fe,Nb)$_{13}$C$_6$
structure, respectively; see also [23]. The Nb-rich specimen contained
a few μ phase particles of up to 5μm in diameter. XRD provided
lattice parameters for the hexagonal C14 Laves phase structures
of $a = 0.48415$ nm, $c = 0.7895$ nm for Fe-33.0 at.% Nb and
$a = 0.48523$ nm, $c = 0.79106$ nm for Fe-35.0 at.% Nb. The observed
increase in the lattice parameters for the Nb-rich off-stoichiometric
Laves phase relative to the stoichiometric composition confirms
previous findings [8–12] of the existence of anti-site atoms in the
Nb-rich alloy. Representative two-beam BF-TEM images are shown in Fig. 3a,b
for the stoichiometric and the Nb-rich alloy. The defect density in
the stoichiometric alloy is significantly lower than that in the Nb-
rich alloy and only isolated defects are observed, see Fig. 3a. In the
Nb-rich alloy, a high density of extended and confined planar
defects is observed as seen in Fig. 3b. A large fraction of the ex-
tended defects span the entire grain with a length of several tens
of μm. Such extended defects appear to be on the basal plane. The
confined defect features are found both on the basal and pyramidal
planes having a length of $\sim$100 to 500 nm. They show fringe con-
trast, which is characteristic of stacking faults and/or plate-shaped
precipitates that are inclined to the electron beam [42].

The atomic structure of the extended and confined defects in
the Nb-rich alloy was further characterized by aberration-
corrected HAADF-STEM. In Fig. 4a-d, a sequence of STEM images
and complementary STEM-EDS elemental maps for Fe and Nb
are presented for the extended defects on the basal plane of the
hexagonal structure. The lower-magnification reference STEM im-
age in Fig. 4a shows a high density of extended defects terminating
at the edge of the thin foil. The atomically resolved STEM image of
one such extended defect in Fig. 4b reveals the presence of a 5-nm
thick slab composed of O units alternating with the Δ and $\varphi$
units. Although these are the characteristic units that make up the
μ phase, their sequence does not correspond to that in a perfect μ phase.
Instead of a $\Delta\Delta\Delta\Delta\Delta\Delta\Delta$ stacking that describes the μ phase,
the sequence here appears quite irregular ($\Delta\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega\Omega$ from bottom to top; also see Fig. 5c later). The slab is fully co-
herent with the host C14 NbFe$_2$ Laves phase on both the top and
bottom interfaces; further, there is no structural disregistry on the
basal plane between the C14 matrix above and below this 5-nm
thick slab, i.e., removing of the slab would result in an undistorted
perfect C14 structure. STEM-EDS data in this region confirm the
presence of the six Fe-poor/Nb-rich O layers (Fig. 4c,d).

In the investigated region of the specimen, various types of
layer-stacking sequence in such thin slabs of “defect” material
(of varying thickness) were recognized; examples are shown in
Fig. 5a-c. In all cases, the slabs consist of alternating O and Δ
(or $\varphi$) layer stacks. The characteristic three-layer arrangement
composed of Nb-atoms in the 4-layer O unit is highlighted in red,
while the Laves-type triple layers with Nb-Fe-Nb arrangement are
marked in green and blue to differentiate between the Δ and $\varphi$
units. The single layer of Fe atoms ordered in a Kagomé net that
forms the fourth layer of each of such triple layers is left uncol-
cored. In all three cases shown in Fig. 5a-c, coherency of the slabs
with the Laves phase matrix above and below the slab can be es-
ablished as well as the lack of disregistry between the Laves phase
matrix above and below the slab along the basal plane. The variant
shown in Fig. 5a is characterized by three-layer stacks of Nb atoms
(in red) and illustrates local twinning symmetry around the cen-
ter Nb plane as indicated by the white arrow. The mirror symme-
try can be noted by observing the triple layer arrangements (blue
and green) in the Δ and $\varphi$ units. This stack can be represented
as $\varphi\Omega\Omega\Delta\Omega\varphi\Omega\Omega\Delta\Omega\varphi$. The defect-slab in Fig. 5b is thicker than the one in
Fig. 5a and consists of four three-layer stacks of Nb atoms (red).
It can be represented as $\Delta\Omega\varphi\Omega\Omega\Omega\varphi\Omega\Omega\Omega\Omega\varphi$ and is indicative of multiple
twin stacking of the units; the white arrows marked in the image
identify the local twinning planes. The variant displayed in Fig. 5c
with six three-layer stacks is the same as that shown in Fig. 4b
that was described above. None of the extended defects discussed
above shows a sequence of stacking that is representative for the μ
phase, although all of them consist of ΔO and $\varphi$O structural units.

![Fig. 2. Back-scattered electron micrographs of Fe-Nb Laves phase alloys with a) 33 at.% Nb and b) 35 at.% Nb. The Nb-rich alloy contains a few μ phase particles (light gray), and both samples show some fine oxide/carbide particles (white, as analysed by TEM in Ref. [23]) along the grain boundaries or in the interior of the μ phase particles.](image-url)
The two-beam DF image in Fig. 6a illustrates a region of the sample containing “confined” defects, i.e., defects bound by partial dislocations within the grain. In Fig. 6b, a LAADF-STEM overview image of this area in the specimen is displayed, and these defects lie on basal and pyramidal planes. An atomically resolved LAADF-STEM image of a “confined” basal defect is shown in Fig. 6c. The increased contrast at the fault is mainly related to lattice strain (and not atomic number contrast) under the given LAADF imaging conditions. Here, although the defect extends across the entire micrograph on the basal plane from left to right, it only extends a few atomic layers in height with a thickness of ~1 nm (the atomic scale structure of this special basal defect will be described in more detail in Fig. 9). Likewise, the pyramidal defect in Fig. 6d extends along the pyramidal plane across the entire micrograph from top.
to bottom, exhibits significant strain contrast and a slab thickness that is a little over 1 nm.

A higher magnification view on the atomic structural units of the pyramidal "defect" is presented in Fig. 7a and a partial dislocation in the vicinity of the termination of the defect at the upper end is shown in Fig. 7b. A closer inspection of the atomic structure of this thin slab in Fig. 7a leads to the conclusion that a perfect μ phase layer has formed in this instance. The three-layer stacks of the O unit and the tripod layers corresponding to the Δ unit are indicated by red arrows and blue lines, respectively. The ABC arrangement of the combined (ΔO) unit confirms the presence of the μ phase unit cell that is repeated along the pyramidal plane; furthermore, this μ phase precipitate plate is fully coherent on the broad faces with the matrix C14 Laves phase. The partial dislocation in Fig. 7b is likely associated with the side face of the plate and shows a highly extended core structure with a radius of >1 nm and within it, segments of the Nb-three-layer stack belonging to the O unit can be observed (marked in red).

The atomic resolution elemental maps in Figs. 7c, d for Fe and Nb establish a significant decrease in Fe X-ray intensity at the three-layer stack of the O unit indicating that, if at all, only a small fraction of Fe atoms partitions into these layers.

A "confined" basal defect, similar to the one in Fig. 6c, and its termination in the C14 phase are shown in the atomic resolution HAADF images of Fig. 8a,b. The thin slab of defective material is highlighted in red in this image and this slab is sandwiched between C14 matrix material that is present at the top and bottom. A careful examination of the image also shows the termination of this defective slab in the middle of the micrograph and the presence of uninterrupted C14 structure on the left side. This region is shown at a higher magnification in Fig. 8b and it is apparent that the transition is not abrupt but appears to occur across a few atomic layers about 3 nm wide. It appears that in the transition region shown in Fig. 8b, both the Kagomé Fe layer and the L-S-L Nb layer of the C14 Laves phase on the left are continuously replaced by a three-layer L-L-L Nb stack of the μ phase. This implies the presence of an extended partial dislocation which accommodates the transition from the perfect C14 Laves phase to the "confined" basal fault.

The atomic resolution STEM micrographs in Fig. 9a,b show images of the "confined" basal defect of Fig. 6c acquired under HAADF (strain contrast) and HAADF (Z-contrast) conditions, respectively. At the defect, a single O unit is observed as indicated in Fig. 9a. The intensity increase in Fig. 9a (LAADF) is resulting from a compressively strained O unit, when considering the equilibrium lattice parameters of the μ and C14 phases. This leads to an intensity decrease in the HAADF image of Fig. 9b, obstructing a qualitative and quantitative contrast interpretation of Nb enrichment. The two parts of the crystal above and below this defect appear shifted with respect to each other in the horizontal direction in the plane of the image by ~80 pm; the lower part demonstrates coherent stacking of the matrix Laves phase and the O unit constituting the defect. Since both Kagomé and L-S-L layer of the C14 phase are replaced by a three-layer L-L-L stack of μ, the stacking sequence is disrupted. When applying the introduced stacking notation in either way from the top or the bottom of the confined basal fault, a full Kagomé layer of Fe atoms appears to be missing (Fig. 9a,b). This can also be seen in the decrease in X-ray
3.2. Theoretical results

Defect types observed experimentally have been investigated by \textit{ab initio} calculations to evaluate their relative stability. The major results are the corresponding formation energies, which are given in Table 1 and discussed in detail in Section 4.2. In addition, these calculations also provide clarification of the atomic configurations observed from the TEM experiments by identifying local energy minima associated with specific structures. As an example of the latter, we discuss below the case of the defect structure with the missing Kagomé layer (shown in Fig. 9a,b) using \gamma\textsuperscript{-}-surfaces.

Of the three variants of extended basal faults shown in Fig. 9a-c, we simulated the one represented as \gamma O\gamma O\gamma (Fig. 5a). The formation energy for this defect termed 'Extended basal' is included in Table 1. Specifically, in the vicinity of this defect, the stacking sequence goes [L-S-L] - S - [L-L-L] - S - [L-S-L]. In our calculation of the formation energy (Table 1), the Kagomé layers right below and above the three-layer stacks of Nb define the coherent interface. To make a coherent basal interface between the two stacking, the a-vector of the \mu stacking (a = 0.4883 nm, c = 2.6734 nm; obtained by \textit{ab initio} calculations for the perfect \mu phase at 0 K) is initially reduced to match the a-vector of the C14 stacking (a = 0.4773 nm, c = 0.7889 nm; obtained by \textit{ab initio} calculations for the perfect C14 phase at 0 K). The corresponding supercells were afterwards fully relaxed in the ferromagnetic state at 0 K.

In constructing the pyramidal stacking fault (experimental image shown in Fig. 7a) not only the volume of the relaxed \mu phase needed to be reduced, but also the c/a ratio is modified to provide a coherent interface with the C14 Laves phase.

Similar to the other defects, the structure of the confined basal fault is discussed as a stacking sequence of structural units, resulting into the apparent absence of a Kagomé layer (Fig. 9a and 9b). An alternative approach, not followed here, would be the analysis of the Fe-K signal with respect to the Nb-L intensity in corresponding STEM-EDS elemental maps acquired at a similar defect and shown in Figs. 9c and d, respectively.

Table 1

<table>
<thead>
<tr>
<th>Structure type</th>
<th>n\textsubscript{\alpha}</th>
<th>n\textsubscript{\beta}</th>
<th>Formation energy (meV/atom)</th>
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<td>C14</td>
<td>8</td>
<td>4</td>
<td>138.3</td>
</tr>
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<td>\mu phase</td>
<td>21</td>
<td>18</td>
<td>125.7</td>
</tr>
<tr>
<td>Extended basal</td>
<td>49</td>
<td>32</td>
<td>126.6</td>
</tr>
<tr>
<td>Pyramidal</td>
<td>61</td>
<td>38</td>
<td>126.7</td>
</tr>
<tr>
<td>Confined basal</td>
<td>20</td>
<td>14</td>
<td>79.6</td>
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<tr>
<td>Kagomé added</td>
<td>23</td>
<td>14</td>
<td>127.3</td>
</tr>
</tbody>
</table>

Fig. 6. (a) Two-beam DF-TEM image of a sample region of the Nb-rich alloy containing confined stacking faults, B = (1101), g = (11–20). (b) Overview LAADF-STEM image of the same sample area containing the confined basal and pyramidal faults, B = (11–20). Atomically resolved LAADF-STEM images of a confined (c) basal and (d) pyramidal fault.
The structural basis for the calculations for this confined basal fault is taken from the atomic resolution STEM images in Figs. 8 and 9. However, these images do not capture possible shifts in the [11–20] direction (perpendicular to the image plane). For a crystal exhibiting hexagonal symmetry, there are only three configurations for the upper interface that satisfy a 60° rotation invariance around [0001]. Since all of those configurations (red, purple, and blue crosses and corresponding insets in Fig. 10a) do not resemble the STEM image, it implies that shifts along the [11–20] direction need to be considered.

To consider a complete set of structures in dependence on the translation vector, the generalized stacking fault energy (SFE) surface or γ-surface was obtained by DFT calculations. The energy landscape for lattice translations in linear combination along the [21–10] and [01–10] vectors of the host C14 structure between the upper and lower part of the missing Kagomé layer were generated.

The relaxed γ-surface plot with \( \Delta d_{\text{cap}}/d_0 = 94\% \) is illustrated in Fig. 10a. All structures up to 4 atomic layers on each side of the missing Kagomé layer were fully relaxed and the rest of layers only relaxed in the [0001] direction to retain the lattice translation after relaxation. The orange line corresponds to all structures that resemble in at least one projection the STEM image in Fig. 9a. After relaxation only structures indicated with an orange-green cross preserved this resemblance. The \textit{ab initio} calculations indicate that the configuration experimentally observed in Fig. 9a is a high-symmetry (saddle) point on the γ-surface, while it corresponds to a local energy minimum in terms of the relaxation of the local atomic coordinates. The result depends, however, on the width of the gap resulting from the missing Kagomé layer as illustrated in Fig. 10b. Only if the gap is a little less than that anticipated from Fig. 9a, can the described metastability of the structure be observed (\( \Delta d_{\text{cap}}/d_0 \leq 96\% \) in Fig. 10b). More precisely, when the distance, \( \Delta d_{\text{cap}} \), of the Kagomé layers bounding the gap is more than 96% the distance of the corresponding Kagomé layers in perfect C14, \( d_0 \), then the minimum on the γ-surface is shifted to a different position. The subsequent relaxation would produce a local atomic arrangement that is not consistent with Fig. 9a and brings the \( \Delta d_{\text{cap}}/d_0 \) to 98%–102% depending on the initial ratios (90%–105%). Nevertheless, a one-to-one comparison to the amount (and even sign) of the strain in experiment is hardly possible. This would require a much more sophisticated consideration of transition pathways, relaxations, magnetism, temperature and Poisson effects than currently done. For example, the relaxation of the internal coordinates for the orange-green cross structures in Fig. 10b increases \( \Delta d_{\text{cap}}/d_0 \) from 92% (95%) to 97% (97%) and reduces the energy by 97 meV (45 meV).

We also performed a calculation, in which we added the missing Kagomé layer to the confined basal stacking fault to compare its energy with the original structure. Since the Kagomé layer influences the basal interface relation between the C14 Laves and \( \mu \)
phases, it turns out that a different lattice translation is required compared to the case of the missing layer which also destroys the resemblance. Therefore, even if adding the missing Kagomé layer lowers the energy, the necessary shearing can result in long-range elastic effects that suppress this process.

### 3.3. Chemical bonding in NbFe$_2$ and Nb$_2$Fe$_7$

An earlier systematic analysis of chemical bonding in Laves phases LS$_2$ has revealed the important role of charge transfer in the stabilization of this structural pattern, which is characteristic for intermetallic bonding. It turned out that the amount of charge transfer is proportional to electronegativity difference between the components of the given Laves phase and to the number of electrons available at the component L [43]. To obtain the absolute values of effective charges for the atomic species in the competing bulk phases, the QTAIM analysis of the calculated electron density was performed. The shape of the QTAIM atom of Nb in the NbFe$_2$ C14 Laves phase is multifaceted, but strongly tends to a sphere (Fig. 11a). This is characteristic for an ionic species like the cations in the Laves phase KPb$_2$ with obviously ionic interaction [43], but was also observed for the cationic species in intermetallic clathrates [44]. Integration of the electron density within the QTAIM Nb atoms yields the population of 40.16 electrons, i.e., a positive effective charge of 0.84. The shape of the Fe entities contains larger plane facets, indicating participation of Fe species in covalent interactions. The two crystallographically different Fe atoms have negative charges of −0.36 (Fe1) and −0.44 (Fe2), respectively (Fig. 11a).

The crystal structure of the Nb$_2$Fe$_7$ μ phase contains three crystallographically different Nb positions. The first one (Nb1) is located within the L-S-L unit characteristic for the Laves phases (Δ). The other two are located within the centre of the L-L-L unit (in the O layer stacking) and on the border between the two structural segments, Nb3 and Nb2, respectively. Accordingly, the Nb1 species have a QTAIM charge (+0.75) very close to that of Nb in NbFe$_2$, while both others reveal clearly reduced charges of +0.49 and +0.48, respectively.

The reason for this charge reduction is a redistribution of the four-center polar heteroatomic and nonpolar homoatomic bonds in both crystal structures. The topological analysis of ELI-D in NbFe$_2$ reveals only four-center (4c) interactions, which are mostly heteronuclear i.e., have contributions of Nb and Fe. The homoatomic bonds 4c-Fe$_4$ are formed in the Kagome network, in agreement with the large plane faces of the iron QTAIM atoms. The polarity of the heteroatomic 4c-Nb$_2$Fe$_2$ bonds (polarity character [49] between 0.28 and 0.34) is not a very strong but distinct one. A similar situation is observed in Nb$_3$Fe$_7$, where the polarity character for the 4c-Nb$_2$Fe$_2$ bonds vary in a slightly larger range from 0.22 to 0.44, depending on the stacking unit in which the bond is located. Therefore, the polarity of the heteroatomic 4c Nb–Fe bonds does not influence the reduction of the effective QTAIM charge of

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**Fig. 8.** (a) HAADF-STEM image of a confined basal fault termination within the C14 matrix; (b) A higher magnification image of the termination indicating a continuous transition from a Δ-type to an O-type atomic ordering. The viewing direction is [1100] for both images and the vertical axis is [0001].
Nb atoms in Nb$_6$Fe$_7$. The main role in this reduction is related to the presence of the non-polar 4c-Fe$_4$ bonds in both segments, and - in particular - the appearance of 4c-Nb$_4$ bonds in the O layer stacking with relatively large populations.

4. Discussion

4.1. Configuration of planar defects

The SEM and XRD microstructures of a stoichiometric alloy with 33 at.% Nb and a Nb-rich alloy with 35 at.% Nb reveal in both cases a C14 NbFe$_2$ structure. However, the comparison of conventional TEM images shows that the stoichiometric alloy is nearly defect-free, whereas a high density of planar defects is present in the Nb-rich sample. Atomic resolution STEM observations confirm that these planar defects incorporate layers of the Nb-rich O units. These planar defects are categorized into extended and confined defects on the basal plane but are also found as confined defects on pyramidal planes. Although by definition in simple crystal structures, a planar defect such as a stacking fault is one atomic layer thick, here these “planar defects” are really “slabs” of structure disruption, extending over multiple atomic layers enabled by the complex atomic stacking sequences. The confined defect that was found on the pyramidal planes of the C14 matrix represents the μ phase unit cell. However, neither the confined or extended defects on the basal plane adhere to any known unit cell nor do they contain repeated units that enable identification of a unit cell. Nevertheless, they capture the O layer stacking of the μ phase to accommodate the excess Nb in this Nb-rich off-stoichiometric alloy.

This observation is going along with – at least it is not in contradiction to – the effective charges obtained from the quantum chemical analysis: The relatively large charge difference between the Nb and Fe positions in the Laves phase NbFe$_2$ involves the danger that an antisite replacement of Fe by Nb would lead to a local overconcentration of positive charges, connected with an energy penalty. The formation of an O layer stacking of the μ phase, on the other hand, yields a local release of the charge stress by reducing the effective charges on Nb atoms.

However, none of the observed variants in Fig. 5 shows a perfect μ phase stacking sequence. It was already hypothesized by Frank and Kasper [1] that many structures are conceivable with different sequences of Δ, γ and O layers. For example, both variants with three- and four-layer stacks of O in Figs. 5a and 5b are in a similar stacking sequence as proposed by Frank and Kasper [1] with alternating ΔOγO layers. Similar structural variants have also been observed in the μ phase in different systems [45,46]. Carvalho et al. [45] report that the occurrence of sub-unit cell twins in μ phases is highly probable and even seems to be an intrinsic feature of μ phases. The confined extension of the thin-slab defects

Fig. 9. (a) LAADF-STEM and (b) corresponding HAADF-STEM image of the confined basal fault of Fig. 6c. The shift of the upper and lower part and the single three-layer stack of the O stack is highlighted in (a). Corresponding STEM-EDS elemental maps for the (c) Fe-K and (d) Nb-L lines. The viewing direction is [11-20] for all images and the vertical axis is [0001].
Fig. 10. (a) The basal generalized stacking fault energy surface (γ-surface) of the structure in the STEM image Fig. 9a, yet with $d_{\text{gap}}/d_0 = 94\%$. The red, purple, and blue crosses (and correspondingly framed structures) are three stackings with 60° rotational symmetry. The orange-green crosses are the structures that resemble even after relaxation in at least one projection (green frame with highlighted unit cell) the STEM image in Fig. 9a and in a projection rotated 60° around [0001] direction another structure (orange frame). The calculated $a_0$ is 0.4773 nm. The unit cell is shown by the black rhombus. (b) Energy profile along the [11-20] direction (orange solid line in a), after initial translation similar to the leading partial dislocation in a synchronshear, though with half of its magnitude (green arrow in a), for which all structures before relaxation have a projection resembling the STEM image of Fig. 9a. The profiles have been generated for different gap widths at the interface, measured as the distance $d_{\text{gap}}$ of the neighboring Kagomé layers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
that capture aspects of the μ phase atomic arrangement in the C14 Laves phase examined in this study encourages the deviation from the perfect stacking sequence to establish a coherent interface with the surrounding C14 Laves phase.

The bright contrast of the pyramidal precipitate imaged under LAADF-STEM conditions of Figs. 6b and d indicates that the μ phase is coherently strained and elastic effects play an important role in dictating the morphological evolution of the precipitates. Any modulation in the stacking sequence of the ΔO structural units would create an interfacial dislocation, which is energetically more costly than maintaining the μ-type stacking. The ends of the precipitate plate are terminated by an extended dislocation core, an example of which is shown in Fig. 7b. Within and in the vicinity of the dislocation core, Nb atoms appear to segregate to and locally reorder, forming the characteristic structural motif of the O layers of the μ phase, and thereby presumably reducing the core energy.

The confined planar basal defect shown in Figs. 8 and 9 is different from the above observations relating to the confined pyramidal planar μ phase precipitate. Here, only a single O layer is present and the stacking sequence along the [0001] direction of the Laves phase is interrupted. An examination of the transition region that constitutes the boundary of this confined defect in Fig. 8b reveals that a full Δ layer of the Laves phase appears to be replaced by an O layer of the μ phase. This transition is partly supported by previous ab initio calculations in a Nb6Ni2 μ phase [47] and by experiments and calculations in a C14 NbCo2 Laves phase [48]. In both cases it is predicted that a favorable site for excess Nb atoms is the S position of the L-S-L triple layer of the C14 Laves and the μ phase. Replacing the small atoms in the single layer Kagomé net was found to be energetically more expensive. It should be mentioned that this view of replacing the Kagomé layer is an oversimplification because the transition from the Δ layer of the Laves to the L-L-L three-layer stack in the μ phase also requires rearrangement of atoms within the planes constituting the fault. The shift between the upper and lower C14 lattice that sandwiches this L-L-L three-layer stack is reminiscent of synchroshear but is more likely zonal glide where the core of the leading partial is spread on more than two adjacent planes. The dislocation core of the partial in the transition region cannot be clearly resolved since the progressive structural transformation enabled in the core complicates the core structure. According to the present DFT calculations, the observed unusual atomic arrangement seems to be locked into a local energy minimum and hence is in a metastable configuration. Furthermore, the disruption in the stacking sequence, and from this perspective, the missing Kagomé layer, opens a gap between the L-L-L three-layer stack of the μ phase and the L-S-L layer of the C14 Laves phase above it. From energetic considerations, only a narrow regime of gap widths (see Fig. 10b), similar to those observed in experiment, provide a stable configuration as otherwise the atomic arrangement in the L-L-L triple layer would not be preserved from destabilizing the defect. The presence of a single three-layer stack of Nb atoms supports
the notion that the characteristic Nb structural motif of the O layer is a stable atomic configuration for Nb atoms in TCP phases, as we also observe them within a dislocation core (Fig. 7b). Similar to the confined pyramidal precipitate, the comparison of the LAADF and HAADF images of Fig. 8 indicates that the O layer is under large compressive strain to establish a coherent interface with the lower part of the C14 phase.

4.2. Phase and defect stability

The structures discussed above are really “slabs of material” where the stacking sequence of the C14 structure is disrupted to accommodate the excess Nb in the alloy. While they may be loosely regarded as stacking faults (planar defects), they do have a three-dimensional characteristic to them and in the case of the pyramidal fault, the slab corresponds to the μ phase unit cell. The Nb enrichment in these slabs is accomplished through O-type atomic ordering. Our stability analysis therefore addresses the question, whether the combination of a planar defect and a bulk-like Nb enrichment confined to a few layers (for example the confined basal fault) is more stable than a separated defect (i.e., the BSSF) in C14 and an extended bulk phase (i.e., large precipitates of μ phase). For a proper comparison of these scenarios, we first present some conceptual considerations (Fig. 12) before coming to the actual results (Fig. 13).

The bulk energies of the considered structures are captured by a convex hull plot as schematically shown in Fig. 12, taking pure ferromagnetic bcc Fe and nonmagnetic bcc Nb as reference states. The formation energies of the stable ferrimagnetic C14 (point A in Fig. 12) and the stable bulk μ phase (point B) are negative (see Table 1) and the solid line connecting points A and B describes the tendency of bulk phase separation. The phase separation (point D) for a certain Nb-enriched, experimentally observed defect structure (point C) into a BSSF defect within the C14 structure (point E) and the μ phase, however, happens according to the thick dashed line.

Our calculations are performed such that the planar defect density (area of defect/volume of supercell) is conserved. This would not be the case, if a linear combination (point F) of the energies for the defect (point E) and the μ bulk phase (point B), as depicted by the dotted line, were performed. Instead, only the part of the supercell containing perfect C14 (blue bar) is replaced by the same volume of μ phase (green bar), independent of the defect area (white plane). By choosing the dashed line parallel to the convex hull, we ensure that the composition gradient reflects the chemical potential of Nb in the equilibrium C14 and μ phases. The artificial extension of the dashed line to the composition of the μ phase (point G) would correspond to the unphysical scenario of a BSSF in this phase.

The DFT calculations for a Nb enriched defect structure need to be performed for artificially high defect densities (point C), due to the limited accessible supercell sizes (Table 1). They therefore need to be rescaled to the experimentally investigated alloy composition (point H) as indicated by the purple line at 0.35 or 35 at.% Nb content. This is achieved by considering an additional contribution of defect-free C14 and performing a linear interpolation between the structures C and A. Consequently, not only the Nb content, but also the defect density and the energy of the defect structures decrease, as indicated by the purple dash-dotted arrow in Fig. 12. Considering also the BSSF in stoichiometric C14 with the same reduced defect density (point J), we now need to compare points H and K for the stability analysis. Note that structure K is a linear combination at 35 at.% Nb of structures J (BSSF) and an unphysical μ phase containing a BSSF (not shown in Fig. 12). This is similar to point D, being a combination of points E and G.

We are now in the position to discuss the calculated DFT energies (Section 3.2) of the experimentally observed structures. The energies provided in Table 1 are represented by large data points in Fig. 13. Following the outlined methodology, the formation energies have afterwards been rescaled to the experimental Nb content (small symbols) and the driving forces of phase separation into a BSSF defect structure and μ phase have been determined (energy difference between points H and K in Fig. 12). Looking at the blue bars in the inset of Fig. 13, all energies are positive, i.e. none of the experimentally observed structures is thermodynamically stable as compared to the phase separation. The energy offset is largest for
the confined basal structure and almost the same for the extended basal and the pyramidal defect.

We note, however, that the µ phase considered as a reference so far, is fully relaxed. This corresponds to the situation of large precipitates of µ phase, involving long-distance diffusion of Nb. Whenever a local chemical equilibrium is achieved, the hypothetically formed precipitates of µ phase would be small. Due to the resulting coherent interface between the C14 matrix and µ phase precipitates and the larger Nb content in the O-type layer of the µ phase, the latter needs to be slightly strained. In case of the basal plane coherent interface, the a and b vectors are constrained and if we assume the c vector of the µ phase to be relaxed (not constrained) then the energy of the µ phase will increase by 16 meV/atom. An isotropic compression of the µ phase, which brings its α-vector to that of C14 and keeping the c/α-ratio constant, will increase the energy by even 34 meV/atom.

These two cases have been added to Fig. 13, giving rise to two new convex hulls (dashed lines). Planar defects like the extended basal stacking faults (not the confined one) are now below the common tangent of C14 and constrained µ. This shows that when we reference in the phase separation to a hypothetical µ phase that is constrained in the basal plane (red bars in the inset of Fig. 13), then the driving force for the phase separation can be slightly negative, i.e. the investigated structures remain thermodynamically stable. The situation is even clearer, if the reference for the µ phase is fully constrained (green bars in the inset of Fig. 13), which explains why these kinds of constrained µ phases are not observed as bulk phase in experiment.

5. Conclusions

In conclusion, we have observed the formation of extended and confined planar defects in a Nb-rich C14 NbFe2 Laves phase by aberration corrected STEM. The stability of these defects is further explored by DFT calculations. The extended defects are <10 nm in thickness, but have a lateral extension of several hundreds of nanometers or more. Atomic resolution imaging confirms that they are fully coherent with the surrounding C14 Laves phase. Each of the defects contains Nb-rich layers, resembling the structural arrangement of the three-layer L-L-L stack of the O unit of the NbFe2µ µ phase. However, none of them represents the perfect ΔO stacking of the µ phase, but instead appear as multiply twinned variants with different layer arrangements of ΔO and γO units. According to DFT calculations, these extended defects are in a stable configuration as compared to the formation of a BSSF defect structure in the C14 Laves phase and a simultaneous accommodative of the excess Nb in correctly stacked, true µ phase precipitates with a constrained basal lattice parameter.

The confined defects appear in two different configurations with basal and pyramidal habit planes. Their lateral extension is <500 nm with a maximum thickness of ~1 nm. The confined pyramidal defect exhibits perfect ΔO stacking of the µ phase and can be regarded as a pyramidal µ phase precipitate. Similar to the extended defects, this thin precipitate is energetically slightly preferred to a µ phase precipitate constrained to the basal plane of the C14 Laves phase.

The confined basal defect shows a disruption in the stacking sequence and can be regarded as a single three-layer L-L-L stack of Nb atoms belonging to the O unit. At its extremity, it appears that a full Δ layer of the C14 Laves phase is replaced by the three-layer L-L-L stack of the µ phase. This layer arrangement does not match any hypothetical stacking sequence. Even though it appears as if a full Kagomé layer is missing, the DFT calculations show that this defect is locked into a metastable configuration.

Declaration of Competing Interest

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

Acknowledgments

The authors would like to thank Simon Voß for providing the two Fe-Nb alloys and Erika Bartsch for the two-beam BF-TEM image of the stoichiometric sample. Furthermore, fruitful discussions with Fritz Körmann, Alvin Ladines, and Ralf Drautz are appreciated. K.S.K. acknowledges the Alexander von Humboldt Foundation for enabling this collaboration. The theoretical contribution was supported by the Deutsche Forschungsgemeinschaft within the joint project DFG HI1300/12 (THL) and DFG HA6047/4-1 (TH.A.). Some of the crystal structures and atomic defect structure models have been drawn using VESTA [50].

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