Origin of phase stability in Fe with long-period stacking order as an intermediate phase in cyclic $\gamma \rightarrow \epsilon$ martensitic transformation

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A class of Fe-Mn-Si-based alloys exhibits a reversible martensitic transformation between the $\gamma$ phase with a face-centered cubic (fcc) structure and an $\epsilon$ phase with a hexagonal close-packed (hcp) structure. During the deformation-induced $\gamma \rightarrow \epsilon$ transformation, we identified a phase that is different from the $\epsilon$ phase. In this new phase, the electron diffraction spots are located at the 1/3 positions that correspond to the (0002) plane of the $\epsilon$ (hcp) phase with 2H structure, which suggests long-period stacking order (LPSO). To understand the stacking pattern and explore the possible existence of an LPSO phase as an intermediate between the $\gamma$ and $\epsilon$ phases, the phase stability of various structural polytypes of iron was examined using first-principles calculations with a spin-polarized formalism of the generalized gradient approximation in density functional theory. We found that an antiferromagnetic ordered 6H$_2$ structure is the most stable among the candidate LPSO structures and is energetically close to the $\epsilon$ phase, which suggests that the observed LPSO-like phase adopts the 6H$_2$ structure. Furthermore, we determined that the phase stability can be attributed to the valley depth in the density of states, close to the Fermi level.

**I. INTRODUCTION**

Austenitic steel is an industrial structural material with a long history. Ever since wear-resistant Fe-Mn-C steel was developed at the end of the 19th century, much attention has been paid to its superior mechanical properties. Among these alloys, those with 28–32 mass percent (mass%) Mn and 4–7 mass% Si are known to demonstrate a shape-memory effect. This effect is governed by a non-diffusive solid-to-solid phase transformation from $\gamma$-austenite with a face-centered cubic (fcc) structure to $\epsilon$-martensite with a hexagonal close-packed (hcp) structure [1]. Plastic deformation and subsequent shape recovery upon heating are associated with the forward $\gamma \rightarrow \epsilon$ and reverse $\epsilon \rightarrow \gamma$ transformations, respectively [2–5].

Figure 1 illustrates the atomic displacement during the $\gamma \leftrightarrow \epsilon$ transformation. The (111) planes in the fcc structure are parallel to the basal (0001) planes of the hcp lattice. The formation of the $\epsilon$ phase from the $\gamma$ phase is induced by stacking faults bounded by Shockley partial dislocations with an $a/\sqrt{6}$ shift on the (111) plane. These partial dislocations occur every two layers in the pathway from the fcc to the hcp structure [6]. This transformation is one of the notable plastic deformation modes in austenite steels. The reversible transformation between the $\gamma$ and $\epsilon$ phases occurs during heating and cooling cycles, and cyclic plastic deformation.

Since researchers showed that a dual-phase magnesium-based alloy with a long-period stacking order (LPSO) structure and $\alpha$-Mg (hcp) exhibited superior mechanical properties and a tensile yield strength of approximately 600 MPa [7], there has been a growth in the development of novel alloys with LPSO structures [8, 9]. In the 1960s, Lysak and Nikolin discovered a phase in a disordered Fe-Mn-C alloy subjected to heating and cooling cycles of 400 $\rightarrow$ –196 °C that was distinct from the $\epsilon$ (hcp) phase [10–13]. The new phase was referred to as the $\epsilon'$ phase. Many LPSO-like phases were later discovered in various Fe-Mn-(Al)-C-based alloys [4, 11, 14–18]. Although the existence of LPSO phases in Fe-Mn-Si-based alloys has also been verified by thermodynamic modeling [19], the actual stacking pattern of LPSO phases has yet to be experimentally identified. In addition, even in pure iron, the phase stability and magnetic properties of the structural polytypes have not yet been studied using first-principles calculations.

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In the present work, transmission electron microscopy (TEM) measurements were performed on Fe-Mn-Si-based alloys subjected to cyclic deformation. Electron diffraction spots at the 1/3 positions that correspond to the {0002} plane of the $\epsilon$ (hcp) phase with 2H structure suggest the existence of an LPSO structure. However, for Fe-Mn-Si-based alloys under cyclic deformation, the observed LPSO phase was unstable during room temperature aging (probably due to sensitivity to temperature variations), and so the structural and magnetic properties of the phase are still unavailable. Therefore, we aimed to determine the most stable stacking configuration of the LPSO structure. The structural and magnetic phase stability of structural polytypes in pure iron were investigated using first-principles calculations based on density functional theory (DFT) [20, 21]. The relative stabilities of the fcc and hcp phases were examined by structural optimization to understand the possible realization of an LPSO phase as an intermediate phase in the $\gamma$–$\epsilon$ transformation.

Antiferromagnetic (AFM) order is crucial in the stabilization of Fe–Mn-based alloy phases with fcc and hcp structures [22–26]. Therefore, we consider all the possible AFM spin structures with collinear spin order, and compare the total energies obtained from non-spin-polarized calculations. The total energies of the candidate LPSO structures are compared to the more stable structure of hcp Fe at 0 K. We discuss the origin of structural stabilities based on the difference in the total density of states (DOS) near the Fermi level.

For the sake of simplicity, pure iron is used as a model for those Fe-rich Fe–X alloys; the amount of alloying element ($X$) is relatively low ($\leq 25$ atom%), and the Fe content is large. The Fe ground state at ambient pressure is widely known to be ferromagnetic with a body-centered cubic (bcc) structure; hcp Fe with a nonmagnetic (NM) ground state only appears under high pressure [27, 28]. In contrast, various hexagonal Fe-rich Fe–X alloys exhibit a wide variety of magnetic states at both ambient and high pressures. Fe-rich Fe–Mn-based alloys with the hcp structure ($\epsilon$ phase) exhibit a Néel temperature of 230 K [29]. $\epsilon$–Fe–X alloys ($X = \text{Ru, and Os}$) have AFM ground states at ambient pressure with Néel temperatures of approximately 100 K. The Fe$_2$Ta alloy exhibits a paramagnetic state in which either an excess of Fe or Ta can induce ferromagnetic ordering at low temperatures (approximately 150 K) [30, 31]. The study of structural polytypes of pure iron will also facilitate investigations into the possibility of metastable phases in such Fe-rich alloys and the new $\epsilon$ phase found in pure iron under extremely high pressures [32, 33].

It is also notable that determination of the ground state for both fcc and hcp Fe from first-principles calculations has proved challenging because the energy difference between different magnetic ordering patterns is constrained to a narrow energy window [34–39]. Magnetic frustration occurs in hcp Fe, where spins are expected to be geometrically frustrated with respect to AFM ordering [40, 41]. Each spin is shared by the eight tetrahedra of the hcp lattice, and the nearest neighbor bonds are shared by the two tetrahedra, as shown in Fig. 2 (a). The ground state spin configuration of the system is formed by the stacking of adjacent tetrahedra. The following two choices are present. Suppose that two spins are antiparallel (between 1 and 2) [Fig. 2(b)], in which case, the two remaining spins (between 3 and 4) should also be antiparallel. However, these axes can be chosen to form an arbitrary angle (an infinite number of ways) with respect to the axis of the first two spins; the ground state is thus infinitely degenerate. If the first two spins form an angle $\alpha$, then the other two spins must form the same angle and be antiparallel with the first two spins [41].

As a result of the geometrical frustration of the spin moments arranged in a tetrahedral configuration in hcp Fe, noncollinear spin order ($\alpha \neq 0$) and spin-intensity modulated (spin-smectic) phases arise as low local minima or saddle points by consideration of an isolated tetrahedron [36–39]. However, previous DFT studies predicted that a collinear AFM state known as type II (AFM-II) has the lowest energy spin configuration of $\epsilon$ Fe at ambient pressure [39, 42, 43]. This collinear spin structure is represented by $\alpha = 0$ [37], and each atom has eight antiferromagnetically coupled and four ferromagnetically coupled neighbors, as illustrated in Fig. 2(c). Their calculated bulk moduli and lattice parameters show better agreement with the recent experimental equation of state (EoS) [44–47], compared to the values obtained from NM calculations. In this study, we have systematically searched for collinear AFM ordering of various
LPSO phases and compare the stability over the total energy of the hcp AFM-II phase.

The paper is organized as follows. The details of the first-principles DFT method are given in Section II. Experimental observations of LPSO-like phases in Fe-Mn-Si-based alloys are presented in Section III. Section IV A describes the calculated structural models for the structural polytypes of Fe. The overall procedure for exploration of the stable AFM patterns is given in Section IV B. The calculated structural and magnetic stabilities are discussed using the EoS in Section IV C. Finally, Section IV D presents an analysis of the DOS for AFM states of LSPO structures to discuss the electronic origin of phase stabilities, followed by our conclusions.

II. CALCULATION METHODS

First-principles DFT calculations were performed using the all-electron full-potential linearized augmented plane wave (FLAPW) method implemented in the QMD-FLAPW12 code [48–50]. This method is known as the most accurate among the first-principles methods. The exchange-correlation functional used was a spin-polarized form of the generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE) [51]. For NM phases, integration of the Brillouin zone was performed using \( k \)-point grids of \( 16 \times 16 \times 8 \) for hcp (2H) Fe, \( 12 \times 12 \times 12 \) for fcc (3C), \( 16 \times 16 \times 4 \) for dhcp Fe, and \( 16 \times 16 \times 4 \) for 6H1, 6H2, and 10H structures. The symbols \( nH \) and 3C represent structural polytypes in Ramboll notation, where \( n \) refers to the stacking period (total number of close-packed planes in the unit cell), and the letters \( H \) and \( C \) denote the hexagonal and cubic lattice types. The number 3 in 3C refers to the stacking period in close-packed layers (ABC), and 3C is the only possible cubic polytype. The subscript in the 6H structures specifies a different stacking configuration of the close-packed planes. The \( K \)-point mesh used for orthorhombic cells with an AFM order of 2H, 6H1 and 6H2 is \( 10 \times 6 \times 4 \), while the meshes for tetragonal unit cells with AFM-S and AFM-D states in fcc (3C) structures are \( 12 \times 12 \times 8 \) and \( 12 \times 12 \times 4 \), respectively. To accurately obtain the electronic structure and the EoS, the cut-off energies for the LAPW basis functions in the interstitial were set to 36 and 310 Ry for the plane waves and potentials, respectively. The common muffin-tin (MT) sphere radius of Fe was set to 1.16 Å for all structural polytypes of Fe. The angular momentum expansion inside the MT sphere was truncated at \( l = 8 \) for Fe atoms. Finally, the method of explicit orthogonalization was used in the present study [52].

III. EXPERIMENT

A. Sample preparation and set-up for fatigue test

A 10 kg ingot of Fe-33Mn-4Si (mass%) alloy was prepared by induction furnace melting in an argon atmosphere. The ingot was hot forged and rolled at an initial heating temperature of 1273 K into a 20 mm-thick plate. The plate was annealed at 1,273 K for 1 h and then quenched in water. The dog-bone-shaped fatigue specimen shown in Fig. 3(a) was machined from the plate, and Fig. 3(b) shows a photograph of the test setup. The axial-strain controlled tension-compression fatigue test was conducted at a total strain-amplitude of 0.01 with a triangular wave at a strain rate of 0.004 s\(^{-1}\) until failure at room temperature. 0.2 mm thick and 3 mm diameter discs were obtained from the fatigue-failed specimen using a low-speed cutter and chemical polishing in a solution consisting of hydrofluoric acid, hydrogen peroxide, and water (1:10:2 by volume). Thin foils for TEM (JEM-4000EX, JEOL; acceleration voltage of 400 kV) observations were prepared by two-step electrolytic polishing using an electrolyte composed of acetic acid and perchloric acid (10:1 by volume) during water cooling.

B. TEM observation of LPSO phase

Here, we present experimental evidence for the presence of an LPSO-like structure in the Fe-Mn-Si alloys after being subjected to low-cycle fatigue failure in a series of studies in a search for a seismic damping alloy [53–55]. Figures 4(a) and 4(b) show a bright-field image and a selected area electron diffraction (SAED) pattern, respectively. The TEM image of the Fe-33Mn-4Si (in mass%) alloy was captured after the sample was subjected to cyclic tensile-compressive loading at room temperature and a constant strain amplitude of 0.01 until fatigue failure; the image depicts a fatigue failed alloy. The SAED pattern in Fig. 4(b) was taken from the encircled area shown in Fig. 4(a).

The \( \gamma \) austenite and LPSO-like phase (\( \epsilon' \) phase) are oriented [011]\( \gamma \) and [2110]\( \epsilon \) to the electron beam direction. The red arrows in Fig. 4(b) show the periodic spots observed at the 1/6 positions between the \{111\}\( \gamma \) spots, which is equivalent to the 1/3 positions that correspond to the \{0002\} plane of the \( \epsilon \) (hcp) phase. These

![Fig. 3. (a) Dimensions of a low-cycle fatigue specimen. (b) Photograph of the fatigue test set-up](image-url)
FIG. 4. (a) Bright-field image and (b) SAED pattern of the LPSO-like (ε′) phase found in the fatigue-failed Fe-33Mn-4Si (mass%) alloy (encircled area in (a)). The red arrows indicate the extra spots at the 1/6 positions that correspond to the (111)γ plane [the 1/3 positions corresponding to the (0002) plane of the ε phase], the latter of which corresponds to the (0006)c′. (c) Dark-field image of (a).

spots show a hexagonal-type structure with a six-layer periodicity of a close-packed plane (6H). The (0006)c′ plane is parallel to the (111)γ plane, and the extra spots are aligned in the c* axis in the reciprocal space. This orientational relationship between the γ austenite and the ε′(6H) phases is identical to the so-called Shoji-Nishiyama (S-N) orientational relationship between the γ and ε (2H) phases [6]. Figure 4(c) shows a dark-field image of the fatigue-failed alloy. The ε′ phase is shown in bright contrast. This image was taken using the (0112)c′ spot, which is encircled and indicated by the double-headed blue arrow in Fig. 4(b). The ε′ phase is highly defective, and the fringes in the bright-field image indicate stacking faults.

Figure 5 (a) shows another TEM image for the LPSO structure taken in a different location of the specimen. In this area, crossing variant plates of the ε′ phase are observed in the S-N orientation. As shown in Fig. 5(b), the (0006) planes of the variants c′1 and c′2 are parallel to the (111)γ and (111)γ planes, respectively. The dark-field images in Figs. 5(c) and 5(d) are taken at the (0113)c′1 and (0113)c′2 spots, respectively. The parallel plates of the c′1 and c′2 phases are shown in bright contrast in the figures. The streaks and the (0001)c′ spots suggest a high concentration of stacking faults in the ε′ planes. The LPSO structure is induced by cyclic deformation; therefore, the crystallographic orientation of the LPSO structure with respect to the parent γ phase should be determined by the deformation axis. The LPSO structures shown in Figs. 4 and 5 have the same six-layer periodicity and differ only in their relative orientation in the γ matrix.

Notably, extra spots were not observed in the initial microstructure, but only in the fatigue-failed specimen after cyclic loading at room temperature. Unlike the Mg alloys with LSPO, the LPSO structure observed in the cyclically deformed Fe-33Mn-4Si (mass%) alloy cannot include the ordering of solute atoms due to their relatively low diffusion rate at room temperature. Therefore, the periodicity can only be caused by the stacking sequence of the close-packed planes, ABC. The extra spots are located at the 1/3 positions that correspond to the (0002) plane of the ε phase with the 2H structure, which indicates that the unit cell has a hexagonal (H) type structure with six-layer periodicity (6H). It has been widely accepted that there are only two such structures without chemical ordering, 6H1 and 6H2, of which the stacking sequences are ABCACB and ABBCBCB, respectively [56, 57]. However, from the TEM measurements, it is still unclear which stacking pattern of 6H is realized in the experimental LPSO phase.

Therefore, first-principles calculations were performed to determine the structural and magnetic stabilities of the 6H structures. In addition, the stabilities of other structural variants, 4H and 10H, were also investigated. As a result, we found that the 6H2 structure, which has an AFM order, was closest in energy to the hcp AFM-II structure. Therefore, it was concluded that the ε′ phase...
most likely has the 6H₂ structure. The structural and magnetic properties obtained from the DFT calculations and the microscopic origin of the phase stability are reported in Sec. IV. It should be noted that plastic deformation modes in the deformation-induced γ–ε transformation can be found in a recent review [55].

TABLE I. Various structural polytypes of Fe. Stacking sequences are characterized by three different notations: Ramsdell, ABC, and hc notations. The symbol ‘‘’ between layers indicates the position of a stacking fault. β represents the hexagonality parameter.

| Type  | ABC       | hc   | β (%) |
|-------|-----------|------|-------|
| 2H (hcp) | AB       | h    | 1.0   |
| 4H (dhcp) | ABC−B−   | hc   | 0.5   |
| 6H₁ | ABCA−C−B− | hcc  | 1/3   |
| 6H₂ | ABC−BC−B− | hcchc | 2/3   |
| 10H | ABC−BC−B−A−C−C | cchhc | 0.3   |
| 3C (fcc) | ABC     | c    | 0     |

IV. CALCULATION RESULTS

A. Structural models of LPSO

We considered six different stacking sequences. The candidate structural polytypes are listed in Table I. The sequences of the 2H (hcp), 4H (dhcp), 6H₁, and 6H₂ structures are ABAB, ABCB, ABCACB, and ABCBCB stacking of close-packed layers, respectively. The stability of the 10H structure—an LPSO structure with a longer period than the 6H structures—was also investigated. The number of possible patterns of the 10H polytype was too large to calculate all the possible structures; therefore, an ABCBCBACAC stacking configuration was used, which has been observed in Mg-Zn-Y alloys [59]. In addition to the ABC notation, we introduce a configurational notation called hc notation to characterize the different stacking variants. In the hc notation, the symbol h represents a local set of three layers in a hexagonal pattern (layers with identical neighbors, i.e., ABA or ACA), and the symbol c represents a set of three layers in an fcc-like pattern (layers with different neighbors, i.e., ABC or BCA) [58]. To characterize the various polytypes, the hexagonality parameter β was employed to represent each LPSO phase as an fcc and hcp composite multilayer using hc notation [60]. This parameter is defined as the ratio of the number of hexagonal layers (nh) to the total number of layers per unit cell: β = nh/(nh + nc), where nh and nc are the respective numbers of h and c blocks in each structure. Therefore, the β values for the end members of the fcc and hcp structures are 0 and 1, respectively, while those of the intermediate polytypes 4H, 6H₁, 6H₂, and 10H are 1/2, 1/3, 2/3, and 0.3, respectively. Later, we discuss the ground state energies of the LPSO phases for both NM and AFM phases as a function of the β parameter in Sec. IV C.

The crystal structures for non-spin-polarized calculations were first generated using periodic boundary conditions to determine their structural stabilities. The theoretically optimized lattice parameters and the internal atomic coordinates are listed in Tables II and III, respectively. In the NM case, the hcp, dhcp, and 6H₁ structures of Fe belong to the same space group (P6₃/mmc); however, the stacking sequence along the z-axis of the hexagonal lattice is different. This stacking sequence means that the lattice constant c in the hcp structure is approximately half that of the dhcp structure. Therefore, the unit cell of the dhcp structure contains four Fe atoms and the 6H structures contain six, while the hcp Fe structure contains two. Of these structures, only the 6H₂ structure belongs to the noncentrosymmetric P6₃m₂ space group. Due to the limitation of symmetry operations, the 10H structure has an orthorhombic cell with the space group Cmcm, and it contains 20 Fe atoms (the primitive cell contains only ten atoms.).

B. Search for the antiferromagnetic order

The stability of the magnetic structure in LPSO phases was also computed from first-principles. Previous DFT studies of hcp Fe have proposed two collinear AFM configurations [42, 43]. First, in the AFM-I configuration, ferromagnetically ordered basal planes of hcp lattice alternate the spin direction. Second, in the AFM-II configuration, the spins alternate along the hcp lattice a-axis, as shown in Fig. 6(a). The latter spin configuration is more energetically favorable than the former [38, 42, 43].

In order to identify stable AFM states for the 6H₁ and 6H₂ structures, we first use the same spin alternation pattern as the AFM-I [Fig. 6(a)] structure in hcp Fe for all (0001)hcp planes (either of type A, B, or C), which provides an in-plane AFM order and offers two possibilities for spin arrangements on this plane (deduced from each other by exchanging up-spins and down-spins). In the framework of the spin-polarized DFT calculations for collinear AFM order, the atomic coordinates with different spins were designated as crystallographically independent sites. Therefore, the in-plane AFM patterns of the hcp lattice must be described by an orthorhombic representation of the hexagonal unit cell [65]. Therefore, for each six-plane LPSO structure, there are 64 (= 2⁶) possible combinations of AFM orders to arrange two types of spin in six basal planes with the in-plane AFM arrangements. Of the 64 possible configurations, the patterns with opposite spin signs were equivalent, so that we obtain 32 patterns per the 6H structure as the possible initial spin configurations. 32 orthorhombic structures containing 12 atoms were thus prepared and their total energies were minimized by spin-polarized DFT calculations. As a result, five and three types of spin configurations were determined for the 6H₁ and 6H₂ structures, respectively. The magnetic moments of all other initial spin configurations were relaxed to zero by the en-
TABLE II. Equilibrium lattice parameters for various structural polytypes of Fe with NM and AFM ordered states along side
the NM and AFM states are shown in Tables III and IV, respectively. The equilibrium lattice volume (zero pressure volume) $V_0$ is given per Fe atom. $B_0$ and $B'$ are the bulk modulus and its pressure derivative, respectively. $\Delta E$ is the relative total energy with respect to that of the AFM-II phase in hcp Fe. The square bracketed items of 3C indicate fixed values in the fit. $c/a$ is the axis ratio normalized to a 2H structure (hcp Fe).

| Type       | Ordering       | Crystal Space group | a (Å) | b (Å) | c (Å) | c/a | $V_0$ (Bohr$^3$/atom) | $B_0$ (GPa) | $B'$ (meV/atom) | $\Delta E$ (meV/atom) |
|------------|----------------|---------------------|-------|-------|-------|-----|----------------------|-------------|-----------------|----------------------|
| 2H (hcp)   | NM             | hex P6$_3$/mmc      | 2.46  | 3.89  | 5.80  | 68.1| 265                  | 111         | 8.58            | 27                   |
|            | AFM-II         | ortho Pmmn         | 2.47  | 4.28  | 3.98  | 1619 | 71.0                 | 190         | 4.95            | 0                    |
|            | Exp. [47]      |                     |       |       |       |     |                      |             |                 |                      |
|            | Exp. [46]      |                     |       |       |       |     |                      |             |                 |                      |
|            | Exp. [45]      |                     |       |       |       |     |                      |             |                 |                      |
|            | Exp. [44]      |                     |       |       |       |     |                      |             |                 |                      |
| 6H$_1$     | NM             | hex P6$_3$/mmc      | 2.45  | 11.85 | 1.613 | 69.2| 279                  | 111         | 4.12            | 80                   |
|            | AFM1           | ortho Pmmn         | 2.47  | 4.20  | 12.02 | 1619 | 71.7                 | 175         | 5.41            | 53                   |
|            | AFM2           | ortho Pmm2         | 2.47  | 4.29  | 12.04 | 1620 | 72.0                 | 183         | 7.21            | 28                   |
| 6H$_2$     | NM             | hex Pnn2           | 2.45  | 11.78 | 1.600 | 69.0| 285                  | 111         | 5.84            | 59                   |
|            | AFM             | ortho Pmm2         | 2.47  | 4.29  | 11.97 | 1611 | 71.5                 | 197         | 4.50            | 15                   |
| 4H         | NM             | hex P6$_3$/mmc      | 2.45  | 7.89  | 1.612 | 69.1| 286                  | 123         | 4.35            | 82                   |
| 10H        | NM             | hex Cmcm           | 2.45  | 4.25  | 19.61 | 1600 | 69.0                 | 283         | 4.43            | 60                   |
| 3C (fcc)   | AFM-D          | tetra P4/mmm       | 2.50  | 2.50  | 7.08  | 71.4| 128                  | 216         | 7.09            | 56                   |
|            | AFM-S          | tetra P4/mmm       | 2.47  | 2.47  | 3.49  | 71.8| 200                  | 216         | 7.19            | 62                   |
|            | NM             | cubic Fm3m         | 3.45  |       |       | 69.2| 279                  | 106         | 4.51            | 106                  |
|            | Exp. [61] (293 K) |                |       |       |       | [79.3] | 133         | 5                  |
|            | Exp. [62] (1273 K) |              |       |       |       | 82.7 | 111         | 5.3                 |
|            | Exp. [63]      |                     |       |       |       | 146 | 4.67              |                      |
| bcc        | AFM            | cubic Iam3m        | 2.83  |       |       | 76.7| 191                  | 54.5        | 4.53            | −57                  |
|            | Exp. [64]      |                     |       |       |       | 166 | 5.49              |                      |
|            | Exp. [63]      |                     |       |       |       | 164 | 5.50              |                      |
TABLE III. Internal atomic coordinates \((x, y, z)\) of NM states for various structural polytypes of Fe. Site represents the Wyckoff positions. The lattice constants that correspond to atomic coordinates are listed in Table II.

| Type | Space group | Site | Atomic coordinates |
|------|-------------|------|--------------------|
| 2H   | \(P6_3/mmc\) | 2c   | \(\frac{1}{3}\) \(\frac{2}{3}\) \(\frac{1}{4}\) |
| 4H   | \(P6_3/mmc\) | 2a   | 0 \(0\) \(0\) |
| 6H₁  | \(P6_3/mmc\) | 2b   | 0 \(0\) \(1\) |
| 6H₂  | \(P6m2\)     | 1c   | \(\frac{1}{3}\) \(\frac{2}{3}\) \(0\) |
|      |              | 2i   | \(\frac{2}{3}\) \(1\) \(0.166\) |
|      |              | 2g   | 0 \(0\) \(1\) |
|      |              | 1f   | \(\frac{2}{3}\) \(1\) \(\frac{1}{2}\) |
| 10H  | \(Cmcm\)    | 4c   | 0 \(0.6666\) \(1\) |
|      |              | 8f   | 0 \(0\) \(0.8489\) |
|      |              | 8f   | 0 \(0.3330\) \(-0.0515\) |
| 3C   | \(Fm3m\)    | 4a   | 0 \(0\) \(0\) |

TABLE IV. Atomic coordinates \((x, y, z)\) of AFM states for various structural polytypes of Fe. \(m_{spin}\) represents spin magnetic moments per atom within the muffin-tin sphere. \(\sigma\) represents the spin index, \(\uparrow\) or \(\downarrow\). Site represents the Wyckoff positions. The lattice constants that correspond to the atomic coordinates are listed in Table II.

| Type | Ordering | Site | Atomic coordinates | \(m_{spin}\) (\(\mu_B\)) |
|------|----------|------|--------------------|----------------------|
| 2H   | AFM-II   | 2c   | \(0\) \(0.3333\) \(1\) | \(0.17\) |
|       | (Pmcn)   | 2c   | 1/2 | \(0.3333\) \(1\) \(1.17\) |
| 6H₁  | AFM₁     | 2a   | \(1/4\) \(-0.2407\) \(1\) | \(0.95\) |
|       | (Pm3m)   | 2a   | 1/2 | \(0.92\) \(0.4138\) \(1.47\) |
|       |          | 2b   | \(-1/4\) \(0.5903\) \(1\) | \(0.95\) |
|       |          | 4f   | \(1/4\) \(0.4081\) \(-0.4138\) \(1.47\) |
| 6H₂  | AFM₂     | 1a   | 0 \(0.2757\) \(0\) | \(1.33\) |
|       | (Pnma)   | 1d   | \(1/2\) \(0.7244\) \(1\) | \(1.19\) |
|       |          | 1h   | \(1/2\) \(0.4088\) \(0.6650\) \(1.40\) |
|       |          | 1h   | \(1/2\) \(0.0912\) \(0.8350\) \(1.38\) |
|       |          | 1c   | \(1/2\) \(0.7757\) \(0\) | \(1.33\) |
|       |          | 1b   | 0 \(0.2244\) \(1/2\) | \(1.19\) |
|       |          | 2g   | \(-0.0912\) \(0.6650\) \(1.40\) |
|       |          | 2g   | 0 \(0.5912\) \(0.8350\) \(1.38\) |
| 3C   | AFM-S    | 1d   | \(1/2\) \(0.1392\) \(0\) | \(1.39\) |
|       | (P4/mmm) | 1d   | \(1/2\) \(-0.1657\) \(1\) | \(1.09\) |
|       |          | 2h   | \(1/2\) \(-0.4904\) \(-0.3359\) \(1.28\) |
|       |          | 2h   | \(1/2\) \(-0.1681\) \(-0.1671\) \(1.38\) |
|       |          | 1b   | 0 \(-0.3508\) \(0\) | \(1.39\) |
|       |          | 1a   | 0 \(0.3333\) \(1/2\) | \(1.09\) |
|       |          | 2g   | 0 \(0.0096\) \(-0.3359\) \(1.28\) |
|       |          | 2g   | 0 \(0.3329\) \(-0.1671\) \(1.38\) |
|       |          | 1d   | \(1/2\) \(0\) \(0\) | \(1.36\) |

The spin intensity of the 6H AFM structures is modulated along the \(c\) axis, as listed in Table IV. The magnitude of the magnetic moment \((0.95 \mu_B)\) in the \(2a\) \((2b)\) site of the 6H₁ structure in the AFM₁ state is much smaller than that of the \(4f\) site \((1.45 \mu_B)\). The results show that the decrease in the magnetic moment is favored by the geometrical frustration and the large spin degeneracy of Fe sites in the tetrahedral geometry. In addition, the frustrated spin state of AFM₁ can change to the more stable spin order of AFM₂, which suggests the effect of spin frustration.
Figure 7 depicts the relative position of the close-packed layers due to the Shockley partial dislocations in the 6H structures. The partial dislocations occur along the b axis of the orthorhombic cells, parallel to the [112] direction of the fcc lattice. An attractive feature is identified in the 6H$_1$–AFM2 structure, in that the direction of the magnetic moment is reversed only in the A layer located at the origin of the c axis, as shown in Fig. 7(a), which indicates that the spin structure has a six-fold period with respect to the Shockley partial dislocation. The change in the direction of the magnetic moments corresponds to the up-spin of the A1 site, while the B1 and C1 sites have down-spins, as shown in Fig. 6(b). The direction of spins does not change for the 6H$_2$–AFM structure with the partial dislocation, as depicted in Fig. 7(b): the magnetic moments at the A1, B1, and C1 sites have the same spin orientation, as shown in Fig. 6(c). However, in the stacking sequence of atomic layers, the A layer appears every six layers, and the other layers are stacked in a BCBCB pattern.

For the fcc structure, two possible AFM states have been reported previously using body-centered tetragonal (bct) lattices [67]. The relationship between fcc and bct cells with (001) type AFM spin patterns is shown in Fig. 8. In both spin arrangements, the magnetic moments are parallel to each other in the (001) plane. However, the first arrangement, termed the AFM single layer (AFM-S), has alternating layers of spin-up and spin-down along the [001] axis. In the second arrangement, double layers with ferromagnetic interlayer coupling are AFM ordered along the [001] direction; therefore, this arrangement is termed an AFM double layer (AFM-D). The magnetic unit cells of AFM-S and AFM-D belong to the space groups P4/mmm and Pmm2, respectively. The c/a ratios for AFM-S and AFM-D are $\sqrt{2}$ and $2\sqrt{2}$, respectively, which corresponds to the fcc structure, and these values are fixed during the structural optimization. These calculations verify the result that the latter AFM pattern is more energetically favorable than the former.

C. Structural and magnetic phase stability

In this section, we discuss the results for the structural and magnetic phase stability of LPSO structures. Table II shows the optimized structural parameters and the total energy differences with respect to the AFM-II state of hcp Fe. Among the NM states of the LPSO candidates, the 6H$_2$ and 10H structures are energetically close to each other; however, the 6H$_2$ structure is the most energetically close to hcp Fe. This result for the NM states is similar to the results of DFT studies for pure Mg, in which the energy difference between various LPSO phases is quite small [68]. On the other hand, the 6H$_1$ structure is less energetically favorable than 6H$_2$, although energetically close to dhcp Fe.

FLAPW calculations with the spin-polarized form of the GGA-PBE functional were also performed, and stable AFM spin structures were determined for the 6H$_1$, 6H$_2$, hcp, and fcc structures (Table II). Several possible magnetic order patterns were also examined for the 4H and 10H structures, including ferromagnetic and ferri-magnetic states; however, no magnetic orderings were stabilized. Therefore, Figure 9 shows only the volume dependence of the total energies for 6H$_1$ and 6H$_2$ that consider AFM ordering and the NM state, as well as those for fcc and hcp Fe. As shown in Fig. 10, the AFM states of the 6H$_1$, 6H$_2$, hcp, and fcc structures are energetically lower than those of the NM phase by approximately 30–
50 meV/atom. Figure 10 also describes the difference of total energy ($\Delta E$) with respect to hcp Fe as a function of the hexagonality, $\beta$. In both the NM and AFM phases, $\Delta E$ decreases almost proportionally as $\beta$ increases.

The equilibrium volumes and bulk moduli are also listed in Table II. The 6H$_2$ structure with AFM ordering is energetically closest to the ground state structure of hcp Fe at ambient pressure. While the 6H$_1$ structure is also stabilized by AFM ordering, the 6H$_1$–AFM1 structure is as unstable as fcc with AFM-D ordering. Nevertheless, the AFM2 state of 6H$_1$ has a lower energy than AFM1, and it becomes energetically closer to the AFM phase of the 6H$_2$ structure. There is a notable energy difference of 13 meV/atom (approximately 150 K) between the 6H$_1$–AFM2 and 6H$_2$–AFM phases. Therefore, we suggest that the LPSO-like phase observed by TEM measurements most likely has the 6H$_2$ structure.

Figure 9 shows the volume dependence of the total energy difference of stacking variants with respect to the AFM-II state of hcp Fe. The equilibrium lattice volumes for the NM states of all the structural polytypes are quite small (69 bohr$^3$/atom), and their bulk moduli (approximately 280 GPa) are generally much higher than the experimental values measured at finite temperatures. The corresponding values for the AFM states are slightly different from each other, which is expected to be due to the magneto–volume effect and spin–spin interactions. When AFM order is considered, the differences of bulk moduli between different types of LPSO become more distinct. As summarized in Table II, hcp Fe with the AFM-II state leads to a better agreement with the experimental bulk modulus within 10% overestimation [45–47] than NM calculations. The calculated bulk modulus for bcc Fe is also slightly overestimated from the experimental modulus [63, 64]. The lattice volume and bulk modulus for the AFM–D state of the fcc (3C) structures are closer to the experimental values (6% underestimation from the experimental bulk modulus at 293 K [61, 62]). While the bulk modulus for the AFM–S state overestimates the experimental values, the equilibrium lattice volume for AFM–S agrees well with those of the hcp, 6H$_1$, and 6H$_2$ structures.

Structural optimization for lattice parameters and internal atomic coordinates was performed for both the spin-polarized and unpolarized calculations. To determine the equilibrium lattice parameters in the ground state at ambient pressure, we first determined the equilibrium volume by specifying the axis ratio of $c/a$ at a constant value, and the calculated total energies at different volumes were fitted using the third-order Birch–Murnaghan EoS. The $c/a$ ratio is optimized by specifying the lattice volume at equilibrium using the fourth-order of the fitting. In Fig. 9, the energy–volume curves are plotted with the $c/a$ ratio optimized at ambient pressure.

FIG. 9. Volume dependence of the total energy difference in structural polytypes of pure iron as a function of hexagonality, $\beta$. $\Delta E$ was calculated with respect to hcp Fe with the AFM-II phase and are listed in Table II. Open and solid circles representNM and AFM states, respectively. The values of $\beta$ are listed in Table I.
D. Origin of phase stabilities

It is also interesting to understand how the stacking sequence along the c axis changes the electronic structure. The DOS for metals with an hcp structure is generally characterized by a deep valley or dip near the Fermi level \( (E_F) \), where \( E_F \) is at the lowest position (the bottom) of the deep valley [69–71]. In the 1970s, before first-principles calculations were established, Inoue and Yamashita suggested that the depth of the valleys in the DOS represents the magnitude of splitting of the main peaks of the DOS between those in the occupied and unoccupied states [69]. This is a type of energy separation between the bonding and antibonding molecular orbitals due to the significant hybridization between the s and p states [69, 72]. From a comparison of the electronic structure of hcp Be and hcp Mg, they also suggested that the degree of energy splitting between the two main peaks (the width of the deep valley or dip) appears as a difference in the enthalpy of formation (or cohesive energies) between the metals [73]. In the early 1970s, it would have been difficult to quantitatively calculate the difference in the heats of formation.

Later, Andersen derived the force theorem, which describes how the change in the total energy of an electron system can be calculated to the first order in a virtual displacement [74]. With this theorem, the energy difference can be simply calculated with DFT as the differences of appropriate sums of the one-electron eigenvalue energies [75, 76]. Therefore, the phase stability analysis based on DOS near the \( E_F \) is effective to understand the energy change associated with small displacement based on the force theorem.

Figures 11(a)–11(d) compare the total DOS for the hcp, 6H2, and 6H1 structures with AFM ordering. A typical deep valley in the DOS observed in hcp metal is evident in Fig. 11(a). The total DOS for the 6H2 structure also has a similar DOS valley near \( E_F \) [Figs. 11(b)], and several small peaks appear near the bottom of these DOS, compared with those for hcp Fe. This is evident in the ABCBCBA stacking of the 6H2 structure, where the A layer appears every six layers, and the other layers are stacked in a BCBCB pattern.

The DOS for the 6H1 structure with the AFM2 configuration is similar to that of the 6H2 phase; however, the \( E_F \) is located at slightly higher energy than the bottom of the valley of the DOS [Figs. 11(c)]. We consider this difference in DOS to be the origin of the energy difference between the 6H1 and 6H2 structures. A comparison of the spin structures of hcp and 6H2 indicates that the local spin arrangement and the stacking sequence agree well with those of the ABAB pattern in the hcp structure. Nevertheless, the total DOS for the unstable 6H1 structure with AFM1 ordering has many peaks near \( E_F \), and the valley of the DOS is obscured [Fig. 11(d)]. We have shown that this deviation of the DOS from the hcp structure is the microscopic origin of the structural stability of the candidate LPSO structures. Based on this analysis, one of the present authors studied the origin of phase stability in an Mg-Zn-Y alloy with LPSO, in which solute elements of Zn and Y were embedded in the Mg matrix near stacking faults [77]. The results will be reported elsewhere shortly.

V. SUMMARY

The structural and magnetic properties of long-period stacking order structures (polytypism) in pure iron were studied by first-principles DFT calculations. During deformation-induced martensitic transformation from \( \gamma \)-austenite to \( \epsilon \)-martensite, a phase (different from the \( \epsilon \) phase) was discovered in Fe-Mn-Si–based alloys. In this phase, the additional diffraction spots are located at the 1/3 positions that correspond to the \{0002\} plane of the \( \epsilon \) (hcp) phase with the 2H structure, which suggests a 6H structure. However, the actual stacking pattern of the 6H phase is unknown. Therefore, we proposed several structural models for the LPSO structure of pure iron, including 4H, 6H1, 6H2, and 10H structures, and structural optimization was performed using first-principles DFT calculations. From a search among the stable magnetic phases, stable AFM states were identified in the 6H1 and 6H2 structures. An AFM state of 6H2 was also revealed as energetically closest to the hcp structure, and the observed LPSO-like phase has a high probability of adopting the 6H2 structure. Due to the probably coherent nature between the possible 6H structures, a negligibly low elastic contribution may not affect the highest probability of the appearance of the 6H2 structure. The electronic origin of the phase stability is attributed to the
depth of the valley in the DOS near the Fermi level; the energy splitting between the two peaks in occupied and unoccupied states is large, which maximizes the phase stability. The relationship between the electronic structure and the phase stability was quantitatively verified for the LPSO and hcp phases in Fe, which was proposed for hcp metals in the 1970s.

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Appendix A: Transformation from a hexagonal unit cell to an orthorhombic unit cell

The crystallographic unit cell (basis) vectors of the orthorhombic cell, \( \mathbf{a}_{\text{orth}}, \mathbf{b}_{\text{orth}}, \mathbf{c}_{\text{orth}} \), are related to those of the hexagonal unit cell, \( \mathbf{a}_h, \mathbf{b}_h, \mathbf{c}_h \), by

\[
\mathbf{a}_{\text{orth}}, \mathbf{b}_{\text{orth}}, \mathbf{c}_{\text{orth}} = (\mathbf{a}_h, \mathbf{b}_h, \mathbf{c}_h) \begin{pmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.
\]