Searching for high magnetization density in bulk Fe: the new metastable Fe$_6$ phase

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Abstract

We report the discovery of a new allotrope of iron by first principles calculations. This phase has $P_{mn21}$, symmetry, a six-atom unit cell (hence the name Fe$_6$), and the highest magnetization density ($M_s$) among all the known crystalline phases of iron. Obtained from the structural optimizations of the Fe$_3$C-cementite crystal upon carbon removal, $P_{mn21}$ Fe$_6$ is shown to result from the stabilization of a ferromagnetic FCC phase, further strained along the Bain path. Although metastable from 0 to 50 GPa, the new phase is more stable at low pressures than the other well-known HCP and FCC allotropes and smoothly transforms into the FCC phase under compression. If stabilized to room temperature, for example, by interstitial impurities, Fe$_6$ could become the basis material for high $M_s$ rare-earth-free permanent magnets and high-impact applications such as light-weight electric engine rotors or high-density recording media. The new phase could also be key to explaining the enigmatic high $M_s$ of Fe$_{16}$N$_2$, which is currently attracting intense research activity.

Keywords: high magnetization density, Fe$_{16}$N$_2$, first principles calculations, iron nitrides, phase stability, Bain strain

(Some figures may appear in colour only in the online journal)
and their higher degree of localization makes Hund’s exchange interaction stronger than for p states. For high $M_s$ applications, 3d TM elements are obviously the most appealing. While permanent magnetism is possible in their compounds (in fact, it was discovered in Fe$_3$O$_4$ magnetite) the presence of other, non-magnetic elements obviously decreases their volume-specific magnetization. In contrast, bulk elemental transition metals are usually soft magnets. Furthermore, the partially itinerant character of their $d$ electrons undermines Hund’s magnetic interactions and contributes to suppressing their bulk magnetization. Nevertheless, there has been a considerable effort to stabilize the useful magnetic phases of transition metals through alloying (for example, Fe–Ni and Fe–Co compounds) or through doping.

Regarding the latter scenario, Fe nitrides have attracted great interest [9–13]. One of the most intriguing Fe–N compounds, Fe$_{16}$N$_2$, has been the object of a sixty year-long debate about the magnetization of its $\alpha''$ ordered phase. The commonly accepted unit cell of this material is a tetragonally distorted $2 \times 2 \times 2$ supercell of bcc iron with nitrogen impurities occupying one fourth of the octahedral interstitial sites. After the crystal structure of this phase was resolved from studying tempered N-doped martensites [14], most of the research on this material focused on the deposition of high $M_s$ thin films, mostly through sputtering. A long controversy was sparked on the magnetic properties of these films. Some groups reported evidence of a saturation magnetization (between 2.4 and 3.2 T) higher than that of $\alpha$ Fe (2.3 T) and exceeding the prediction of the Slater–Pauling theory [15–18]. Others failed to observe any deviation from the trend established by this theory based on itinerant magnetism [19–21], also obeyed by other Fe nitrides [22–26]. Recently, the interest in this material was renewed by the research by J-P Wang’s group. This group was able to deposit a thin film of Fe nitride with a Fe–N stoichiometry close to 8:1, which, after proper annealing, reproducibly showed a magnetization density exceeding 2.68 T [10, 27–29].

All the ab-initio calculations performed in the last decade on this material have been based on the crystal structure proposed by Jack [14], and have failed to find a higher $M_s$ than bulk Fe, even when using corrections to the DFT functionals (such as DFT + U, or hybrid functionals) able to improve the description of electronic localization on $d$ states [30–37]. The only exception remains the model proposed by Wang’s group [38], based on the existence of Fe$_{16}$N super-magnetic clusters with additional Fe atoms in their interstitials.

The present work is motivated by the controversial magnetic properties of this system. However, in this paper we deviate from the common approach of other works in the literature and question the ability of the tetragonal $\alpha''$ of Fe$_{16}$N$_2$ to express a high magnetization density. While Wang’s experiments [10, 27–29] suggest that the ordering of nitrogen impurities (achieved through annealing) probably plays a key role in determining the magnetic properties of the obtained crystal, the rich variety of Fe–N stoichiometries and the abundance of alternative crystalline phases open other possibilities that are worth considering. The idea we started exploring with the present paper is to obtain a crystal with a 16:2 stoichiometry from the superstructures of other suitable Fe nitrides, whose nitrogen concentration is then properly adjusted. Following this line, we discovered a new (metastable) allotrope of iron, which shows the highest $M_s$ of all known phases. This new crystal of iron could represent a first step towards the rationalization of the high $M_s$ of the $\alpha''$ phase of Fe$_{16}$N$_2$ and is the main focus of the present paper.

The results presented here are based on density-functional-theory (DFT) [39, 40]. The technical details of these calculations are briefly summarized in the footnote.

Our investigation started from a preliminary screening of the saturation magnetization density of different Fe nitrides, whose results are shown in figure 1. Based on the possibility of reaching higher values of $M_s$ within the Fe–N family of compounds (red line), this stoichiometry was adopted as the starting point. However, due to the scarce resemblance to the tetragonal structure of the $\alpha''$ phase, the hexagonal Fe$_3$N was disregarded. On the other hand, the tendency of C-doped Fe to form, upon slow cooling from the $\gamma$ fcc solid solution, an orthorhombic crystal with the same C content (Fe$_3$C cementite) suggested the use of this structure as a starting point. Fe$_3$C

Figure 1. Magnetization density (in Tesla) of several Fe–N compounds at zero pressure. The lines are a guide for the eye. From left to right the blue diamonds represent bcc Fe, Fe$_6$N, Fe$_{16}$N, Fe$_{24}$N, Fe$_{32}$N, Fe$_{54}$N, and Fe$_{108}$N$_2$. The red triangles represent hcp Fe, Fe$_{32}$N, Fe$_{54}$N, and Fe$_{108}$N$_2$. The green squares are relative to the orthorhombic crystals and represent Pnnm$_2$, Fe$_{12}$N, Pmnm Fe$_{16}$N, and Pnma Fe$_{32}$N cementite (see text).
Figure 2. Crystal structures of (a) cementite Fe₃N, (b) Pmnmn Fe₀, (c) Pmn2₁ Fe₀ at 0 GPa, and (d) Pmn2₁ Fe₀ at 70 GPa, which is identical to fcc Fe. The orange and blue spheres denote iron and nitrogen, respectively. The upper, middle, and lower rows correspond to the [0 0 1], [1 0 0], and [0 1 0] views of the cementite crystal in column (a), to the [0 1 0], [0 0 1], and [1 0 0] views of the Pmnmn Fe₀ crystal in column (b), and to the [1 0 0], [0 1 0], and [0 0 1] views of the Pmn2₁ Fe₀ crystals in columns (c) and (d).

cementite has a unit cell containing four formula units (shown in figure 2(a)) and a Pnma space group. Its structure and symmetry are preserved when carbon is replaced by nitrogen, which results in a marginal volume increase. Although the unit cell of the cementite structure (Fe₁₂N₄) is not easily matchable with the 8:1 stoichiometry, it was used to qualitatively study the effect of nitrogen removal on the magnetic and structural properties of the crystal. In Pnma Fe₃N nitrogen atoms occupy the center of the trigonal prisms of iron, and are six-fold coordinated. The magnetic moment (per atom) and magnetization density of Fe₃N are relatively low: 2.05 \( \mu_B/Fe \) and 1.81 T, respectively. The removal of one nitrogen per cell does not significantly affect the structure of the crystal. Instead, when two or more nitrogen atoms are subsequently removed from the unit cell, giving Fe₆N, Fe₁₂N, and pure Fe, respectively, structural optimization leads to a drastic change in the crystal structure.

The Pmnmn crystal structure, obtained on the extraction of all the nitrogens from Pnma-type Fe₃N, is shown in figure 2(b). Due to a translational symmetry, not present in the original Pnma crystal, the unit cell of the Pmnmn Fe is half the size of that of cementite, with six atoms instead of twelve (hence the name Fe₀). The rest of this paper will be dedicated to discussing the properties of the Fe₀ crystal.

The Pmnmn crystal was obtained by a naturally symmetry-preserving structural optimization [41]. Its phonon dispersions, reported in figure 3(a), still indicate the presence of unstable modes in the vicinity of \( \Gamma \) and \( Y \) points in the Brillouin zones. Structural re-optimizations along the pattern of atomic displacements of the unstable zone-center mode produces a new structure with symmetry Pmn2₁, as shown in figure 2(c). This structure is dynamically stable, as proved by the absence of imaginary frequencies in its vibrational spectrum (see figure 3(b)). To the best of our knowledge this allotrope of iron has not been reported in the literature.

The new phase crystal structure is shown in column (c) of figure 2. As is evident from the top figure, it presents a three-fold modulation on the (0 0 1) planes with a symmetric (two-to-one) ‘zig–zag’ alternation of distorted Fe quadrangles. If one orientation of distorted quadrangles is prevalent on one (0 0 1) plane, the opposite occurs on the neighboring parallel planes. The resulting ABAB stacking along [0 0 1] prevents the formation of mirror planes in the crystal. A comparison with Pmnmn Fe₀ (column (b) of figure 2) highlights the relationship between the two structures and the deformation induced by the optimization of the Pmnmn crystal along its \( \Gamma \) soft mode. The space group of the new optimized structure, Pmn2₁, is a subgroup of Pmnmn. Hereafter, we refer to this new phase as ‘Pmn2₁ Fe₀’. The lattice parameters and atomic positions for the Pmnmn and Pmn2₁ Fe₀ crystals are reported and compared in table 1 using the Wyckoff notation.

Since the total energy at 0 GPa obtained for this phase is 4.2 mRy/Fe higher than that of the ferromagnetic (FM)
Figure 3. Phonon dispersions at 0 GPa of (a) interim $Pmmn$ Fe$_6$ and (b) $Pmn2_1$ Fe$_6$.

Table 1. Calculated lattice constants and atomic Wyckoff coordinates $x, y, z$ of $Pmn2_1$ and $Pmmn$ Fe$_6$ at 0 GPa. The $(2a)$, $(2b)$, and $(4f)$ positions are given by $\{(0, y, z), (1/2, -y, z + 1/2), (0, 1/2, 0, -z), (x, 0, z), (-x, 0, z), (x + 1/2, 1/2, -z)\}$, and $(x + 1/2, 1/2, -z)$, respectively.

| Structure | $(a, b, c)$ (Å) | $Pmn2_1$-type Fe$_6$ | $Pmmn$-type Fe$_6$ |
|-----------|-----------------|----------------------|----------------------|
|            | $(a, b, c)$ (Å) | $(4.032, 2.464, 7.197)$ | $(7.252, 4.026, 2.460)$ |
| Fe$_1$     | $(2a)$          | $(0, 0.07044, 0.75564)$ | $(0, 1/2, 0.93204)$ |
| Fe$_2$     | $(2a)$          | $(0, 0.25046, 0.08932)$ | $(0.83069, 0, 0.33549)$ |
| Fe$_3$     | $(2a)$          | $(0.42873, 0.42311)$ |

bcc crystal, $Pmn2_1$ Fe$_6$ is a metastable phase of iron. Its $M_s$ (2.47 T) is the highest ever reported for any (meta)stable allotrope of this elemental metal. The unit cell of $Pmn2_1$ Fe$_6$ can be understood as derived from a $1 \times 3 \times 1$ supercell of a conventional bcc structure (simple cubic lattice with a two-atoms basis) with a slight contraction along [0 1 0] ($b/a \sim 2.92$), a substantial elongation along [0 0 1] ($c/a \sim 1.65$), and a significant readjustment of ionic positions, producing the above-mentioned structural modulation.

Indeed, the appearance of metastable modulated phases along the Bain deformation path from the high-temperature austenite to the low-temperature martensite phases is not uncommon in materials undergoing martensitic transformations. In $Pmn2_1$ Fe$_6$, however, the $c/a$ ratio exceeds that of fcc ($c/a = \sqrt{2}$), thus preventing its classification as an intermediate phase between bcc ($c/a = 1$) and fcc. Figure 4 shows the volume-preserving deformation energies versus $c/a$ of (a slightly deformed) $Pmn2_1$ Fe$_6$ (orange line) and of a $1 \times 3 \times 1$ supercell of conventional bcc/bct structure (blue line). The volume, equal to that of the equilibrium structure of $Pmn2_1$ Fe$_6$, is 3.8% larger than that of the bcc structure at equilibrium, and 2.3% smaller than that of the fcc crystal optimized with a FM configuration. As can be seen in the figure, the tetragonal deformation of the bcc cell results in a double-well energy profile in which the bcc structure ($c/a = 1$) represents the global minimum, the fcc ($c/a = \sqrt{2}$) the central maximum, and a bct cell with $c/a \sim 1.64$ (compatible with that of $Pmn2_1$ Fe$_6$) the second (local) minimum. The orange curve in the figure is obtained by changing the value of $c/a$ in an orthorhombic cell with atomic positions compatible to those of the modulated $Pmn2_1$ Fe$_6$ structure and $b/a = 3$, instead of the equilibrium value 2.92, for a better comparison with the bcc supercell. This curve has only one minimum, in correspondence of the Fe$_6$ cell, which is deeper than the local
minimum of the distorted bcc supercell energy profile. The two energy curves cross-over in correspondence with the fcc structure, which thus plays the role of a saddle point between the bcc and the \(Pmn2\) \(Fe_6\) basins at zero pressure.

Being obtained from a ferromagnetic crystal, \(Pmn2\) \(Fe_6\) also has an FM ground state. Its AFM and non-magnetic (NM) phases (the latter is actually coincident with fcc, as discussed below) have energies 36 and 75 mRy/atom higher than that of the FM phase, respectively. The magnetic moment and magnetization density of this phase are, respectively, 2.55 \(\mu_B/Fe\) and 2.47 T, significantly higher than those of the bcc phase (2.34 \(\mu_B/Fe\) or 2.33 T). In fact, to the best of our knowledge, these values are the highest ever reported for any allotrope of Fe. In order to understand the origin of the high magnetization density it is useful to study how this quantity changes with \(c/a\) for the two types of distorted cells considered above. The results, as shown in figure 5, indicate that the bcc supercell has a higher magnetization density than \(Pmn2\) \(Fe_6\) for all the considered values of \(c/a\), except those in the close vicinity of the \(Fe_6\) stability basin, where the two curves essentially coincide. This observation clarifies that the modulation in the \(Pmn2\) \(Fe_6\) structure, i.e. the shifting of the atoms from their bcc equilibrium positions, is only responsible for the stabilization of the \(Fe_6\) orthorhombic crystal, but plays a very marginal role in the on-set of its high magnetization. The deviation of \(b/a\) from 3 also has negligible effects on \(M_s\). The high magnetization density is, instead, mostly due to the elongation of the \(c\) axis, which transforms the bcc into a bct cell with \(c/a \sim 1.64\). This distortion of the bcc structure changes the order (in energy) of the 3d states of iron and allows their occupancies to conform to Hund’s rules more closely, thus enhancing the magnetization. It is important to note that the FM fcc structure has the highest \(M_s(\sim 2.53\) T) out of all the phases considered in this study; at the same time, the bcc structure (\(c/a = 1\)) corresponds to the minimum of \(M_s\) along the bcc curve. Because of deviations from their equilibrium volumes, the ground state values of \(M_s\) for bcc and FM fcc are different from those reported in figure 1 and result in 2.33 T and 2.56 T, respectively.

The magnetic ground state of fcc Fe has been reported to be non-collinear, and to consist of a spin spiral incommensurate with the lattice [42, 43]. The spin modulation of the fcc phase represents an intriguing counterpart of the structural modulation that leads to \(Pmn2\) \(Fe_6\) and stabilizes an FM ground state. To further investigate this aspect, we decided to analyze the vibrational spectrum of the FM fcc crystal. The obtained phonon dispersions indicate the presence of two soft modes along the \(\Sigma\) and \(\Lambda\) lines (see figure 6). The soft modes along the \(\Lambda\) line are not very interesting to the present study. In fact, optimizing the unit cell with an ionic displacement pattern corresponding, for example, to the imaginary-frequency mode at \((1/6, 1/6, 1/6)\) merely evolves the fcc structure into the bcc one, along the very well-known Bain deformation path. The soft modes along the \(\Sigma\) line are, instead, more interesting. The largest imaginary phonon frequency (∼70 cm\(^{-1}\)) occurs at \((\xi, \xi, 0)\) with \(\xi \sim 0.4\). To clarify the nature of the structural deformation induced by this soft branch, we studied the soft vibrational mode at \((1/3, 1/3, 0)\), the closest to the minimum of the soft phonon line that is compatible with a supercell of reasonable size \((3 \times 3 \times 1)\). By optimizing this supercell of the fcc crystal with atoms moved from their equilibrium positions according to the displacement pattern of this soft mode, a three-fold modulated array of distorted Fe octahedra is obtained. The FM fcc phase transforms into the interim \(Pmmm\) structure, as shown in figure 2(b) and, eventually, into \(Pmn2\) \(Fe_6\), thus highlighting its direct connection with this allotrope. The position of the FM fcc crystal at a saddle point of the energy profile between the bcc and the \(Fe_6\) structures, which emerged from figure 4, is thus fully confirmed by the study of its vibrational properties. The presence of a whole band of soft modes along the \(\Sigma\) direction of the Brillouin zone indicates instabilities in the FM fcc crystal at all length scales. The ability to undergo structural distortions, either commensurate, such as the one leading to \(Pmn2\) \(Fe_6\), or incommensurate, could probably be understood as the structural counterpart of the incommensurate magnetic structure (spin-spiral) of the fcc crystal [42, 43]. In short, while a perfectly periodic fcc crystal is characterized by an incommensurate spin-spiral order, an FM ground state can be only stabilized by structural modulations with various periodicities.
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Pmn
21, Fe6, a collinear-ferromagnetic fcc phase represents an intermediate maximum of the energy (a saddle point) between the bcc and the Pmn
21, Fe6 phases, and corresponds to the largest Bain deformation that does not produce a modulation of atomic positions. This picture is confirmed by the instability of fcc towards both bcc and Pmn
21, Fe6.

Owing to its high magnetization density, a stabilized Fe6 could be the starting point for designing materials with a possibly high magnetic coercivity, for highly technological applications such as, for example, lighter-weight electrical engine and power generator rotors, or high information density recording media. In fact, it would be interesting to verify whether a high magnetization-density material can be obtained from Pmn
21, Fe6 by adding nitrogen impurities and, in particular, with a stoichiometry close to that of Fe16N2. Unfortunately, the dimensions and the complexity of the needed supercell makes this idea quite challenging to test computationally. From the abundant literature on iron and its well-consolidated metallurgy, there seems to be little/no evidence that an FM fcc phase can be stabilized at room temperature through the addition of doping impurities (except, perhaps, in nanoparticles [46]). However, re-interpreting the structure of α′′ Fe16N2 as a stabilized fcc supercell could provide a key insight into explaining its enigmatic giant Mγ, and will be the object of future investigations.

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Figure 7. Relative enthalpies of several iron allotropes with respect to bcc Fe iron.

It is important to keep in mind that the volume of the FM fcc phase considered above is larger than that of its non-magnetic counterpart, and of both the bcc and Fe6 phases. In order to clarify how their relative stability changes with volume, and to better understand the relationship between the Pmn
21, Fe6 crystal and the other phases of Fe, it is useful to study the behavior of this allotrope under hydrostatic pressure. Figure 7 shows the enthalpies of the different crystalline structures of Fe (with the FM bcc taken as reference) for pressures between 0 and 50 GPa. At 0 GPa Pmn
21, Fe6 is more stable than all the other allotropes, and its total energy is 2.9 mRy/atom lower than that of the AFM type-II hcp crystal, a high-pressure form of pristine iron [44] and, up to now, the second most stable phase, after bcc. Finite temperature effects, accounted for by including vibrational terms into the free energy, for example within the quasi-harmonic approximation [45], hardly affect the stability. The Pmn
21, Fe6 remains metastable with respect to the bcc phase at lower pressures. Its free energy at 300 K is 3.9 mRy/atom higher than that of bcc Fe and, even if quantitative details, such as transition pressures, may change with temperature, the overall qualitative picture emerging from figure 7 remains unaltered.

Under pressure Pmn
21, Fe6 undergoes a magnetic transition into an AFM phase (at ∼15 GPa), followed by a continuous transformation into the NM fcc phase, completed at ∼40 GPa. Thus we can evince a sort of ‘magneto-structural duality’ between Pmn
21, Fe6 and fcc Fe: While the FM ground state of the fcc phase can be stabilized by a three-fold modulation compatible with the structure of the Pmn
21, Fe6, Pmn
21, Fe6 transforms into fcc under pressure, upon losing its magnetization.

In summary, we found a new metastable allotrope of bulk Fe that is characterized by a unit cell of six atoms with a Pmn
21, space group, and a magnetization density higher than any other known phase. Investigation of this structure highlighted its connection with the bcc and fcc crystals, and showed that it can be obtained from a modulation of a 1 × 3 × 1 bcc supercell after imposing an elongation of the c axis up to c/a values of ∼1.64. Along the extended Bain deformation path, which transforms the bcc structure into the Pmn
21, Fe6, a collinear-ferromagnetic fcc phase represents an intermediate maximum of the energy (a saddle point) between the bcc and the Pmn
21, Fe6 phases, and corresponds to the largest Bain deformation that does not produce a modulation of atomic positions. This picture is confirmed by the instability of fcc towards both bcc and Pmn
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