

The β β - Iron Controversy Revisited

| | |
|-------------------------------|---|
| Journal: | <i>Journal of Phase Equilibria and Diffusion</i> |
| Manuscript ID | JPED-18-03-2079.R2 |
| Manuscript Type: | Research Article |
| Date Submitted by the Author: | 13-May-2018 |
| Complete List of Authors: | Laughlin, David; Carnegie Mellon University, MSE |
| Keywords: | beta iron, ferromagnetic phase, iron, magnetic symmetry |
| | |

SCHOLARONE™
Manuscripts
View Only

The β – Iron Controversy Revisited

David E. Laughlin
ALCOA Professor of Physical Metallurgy
Carnegie Mellon University
Pittsburgh, PA USA

Abstract

Early twentieth century Fe-C phase diagrams designated the paramagnetic BCC iron phase (ferrite) as β iron. By the third decade of the last century this designation all but disappeared from the literature. Why was this? Should the β phase of iron be brought back to phase diagrams? What effects on the phase diagram would arise if we differentiate the ferromagnetic magnetic phase (α) from the paramagnetic phase (β)? In this paper I will discuss some of the history of this β iron controversy and discuss the effects on the Fe-C binary phase diagram. I will urge that β iron should be returned to iron phase diagrams so as to better represent a proper view of magnetic phase equilibria, magnetic symmetry and magnetic phase transformations.

1. Introduction

A glance at the Fe-C binary phase diagram reveals interesting and enigmatic features [1]. The low temperature iron rich phase is not a close packed structure which we are used to seeing in binary phase diagrams at low temperatures (either FCC or HCP) but rather is a phase usually designated as BCC α iron. Even more intriguing is the replacement of this BCC phase at 910 °C (1183K) by an FCC one (designated as γ iron) and the subsequent reappearance at 1391 °C (1664K) of the BCC phase at higher temperatures, designated as the δ phase. Another interesting feature is that in the modern phase diagrams the phases are labeled α , γ and δ (and ϵ if high pressures were included in the diagram) but no β phase? Why is this?

1
2
3 In an earlier paper Massalski and Laughlin [2] discussed the thermodynamic
4 reasons for the low temperature phase not being the FCC phase, and why the
5 paramagnetic BCC phase is replaced by the FCC one at higher temperatures. We
6 accounted for this interesting behavior in terms of the magnetic moments
7 associated with the Fe atoms, including the little known fact that at temperatures
8 below $\approx 70\text{K}$, metastable FCC γ iron becomes anti-ferromagnetic. The added
9 entropy due to the antiferromagnetic to paramagnetic transition at low
10 temperatures is what enables γ iron to replace the BCC phase at higher
11 temperatures. Massalski and Laughlin also discuss the “missing” β phase and
12 make a plea to reinstate it on the phase diagrams of iron based alloys.
13
14
15
16
17
18
19
20
21

22 In this paper, I will review some of the history of the β phase of iron and give the
23 stated reasons for its excising from the phase diagram. After criticizing the reasons
24 that have been given for its exclusion from the phase diagram, I will make a case
25 for reinstatement of the β phase to phase diagrams as the paramagnetic BCC phase
26 of iron. Some salient features of including the magnetic state of the phases on the
27 equilibrium Fe-C phase diagram will be discussed.
28
29
30
31
32
33
34

35 **2. Overview of the history of the β phase¹**

36
37 The α and β phases were named by Osmond and Werth in 1885 [4, 5]. In later
38 papers [6-8] Osmond reported on thermal arrest temperatures he called A_r (on
39 cooling) and A_c (on heating). The A_{r3} and A_{c3} temperatures correspond to the
40 critical temperatures on cooling and heating respectively of the transformation
41 between what we call today the FCC γ phase (paramagnetic) and the BCC
42 paramagnetic phase. The temperatures A_{r2} and A_{c2} (which were nearly identical)
43 correspond to the transformation of the BCC paramagnetic phase to the
44 ferromagnetic α phase, and vice versa. Today we call this temperature the Curie
45 temperature ($770\text{ }^\circ\text{C}$, 1043K), after Pierre Curie, (1859 – 1906).
46
47
48
49
50
51

52
53 ¹ I have gleaned many of the references in this section from the paper by Cohen and Harris, “The β -
54 Iron Controversy” [3].
55
56
57
58
59
60

1
2
3
4
5
6 Based on these results the phase diagrams of iron alloys in the early decades of the
7 20th century, the solid state phases of iron were delineated as
8

9 α , for the low temperature ferromagnetic phase,

10
11 β , for the BCC paramagnetic phase which forms from α at the Curie
12 temperature (A_{c2})
13

14
15 γ , the FCC paramagnetic phase which forms from β at ~ 910 °C (1183K), the
16 A_{c3} .
17
18

19
20 Later, the high temperature BCC phase which formed from the γ phase on heating
21 discovered by Honda [9] was called the δ phase. Thus the solid state phases of
22 iron were delineated as shown in Fig.1.
23
24
25
26
27

28 This delineation of the phases of iron implied that iron existed in three distinct
29 polymorphs or allotropes, namely those designated as the α , β and γ . It was
30 realized that the δ phase was a continuation of the β phase: both were BCC and
31 both were paramagnetic. In fact the plot shown in Fig. 2 of the inverse of the
32 magnetic susceptibility of Fe *versus* temperature shows that the susceptibility of
33 the δ phase is a continuation of that of the β phase. It also shows that at the A_{r2}
34 temperature (Curie temperature) the magnetic properties of β iron changed
35 discontinuously when it is cooled through the Curie temperature and that when β
36 iron transforms to α iron, the iron becomes a ferromagnetic phase.
37
38
39
40
41
42

43 So why was β extracted from the phase diagram? A little more than five decades
44 ago, Cohen and Harris [3] wrote an article entitled “The β – Iron Controversy”. In
45 a clear and concise fashion the authors reviewed the history of the β – Iron
46 “controversy”. They first discussed some of the properties which had been
47 attributed to β iron, such as its effect on hardness etc. After clearing up these
48 erroneous concepts (which the present paper does not discuss) they moved onto the
49 idea that α and β iron were different allotropes of iron, and made their opinion
50
51
52
53
54
55
56
57
58
59
60

1
2
3 clear: β should not be included in modern phase diagrams of iron and its alloys
4 because the “so-called α to β transition” is not a phase transition.
5
6

7 This statement has as its basic underlying assumption that the α and β states of Fe
8 are the same phase. This is said, even though the two states have very different
9 magnetic properties. This implies that properties of the states do not enter into the
10 definition of a phase. Now this is a strange approach as nearly all definitions of
11 thermodynamic phase includes the uniformity and specificity of physical and
12 chemical properties. As far back as 1923 in their highly influential text
13 “*Thermodynamics and the Free Energy of Chemical Substances*’, Lewis and
14 Randall [10] define a phase as:
15
16
17
18
19

20 a homogeneous region of matter in which its properties are the same or at
21 least vary continuously from point to point.
22
23

24 The same may be seen from Professor Christian’s rather complete description of a
25 phase:
26
27

28 “... an assembly of atoms or molecules which has attained equilibrium under
29 specified external constraints consists of one or more homogeneous and
30 physically distinct regions. The regions of each type may be distinguished by
31 a common set of parameters defining such intrinsic properties as density,
32 composition, etc. and they constitute a *phase* of the assembly. Two phases are
33 distinguishable if they represent different states of aggregation, different
34 structural arrangements in the solid, or have different compositions”[11].
35
36
37
38
39

40 More recently Soffa and Laughlin [12] define a phase as:
41

42 “.. a physically distinct homogeneous portion of a thermodynamic system
43 delineated in space by a bounding surface, called an interphase interface, and
44 distinguished by its state of aggregation (solid, liquid or gas), crystal
45 structure, composition and/or degree of order. Each phase in a material
46 system generally exhibits a characteristic set of physical, mechanical and
47 chemical properties and is, in principle, mechanically separable from the
48 whole.”
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 So on the basis of the drastic change in magnetic properties, the α to β
4 transformation should be designated as a phase change and thus α and β would be
5 different allotropes of iron.
6
7

8
9
10
11 It is at this point that the real problem seems to have raised its head. Allotropes are
12 said to have different crystal structures and α to β iron were thought to have the
13 *same crystal structure*, namely BCC. This was believed to have been shown by
14 some very careful high temperature x-ray diffraction of Westgren and Phragmén
15 reported in 1922 [13]. The x-ray patterns for the purported α and β phases (at 16
16 °C and 800 °C respectively) seemed to be identical except for the shift in spacing
17 due to thermal expansion. Since the crystal structures were the same the phases
18 were said to be the same. Thus, it was concluded there was no phase
19 transformation and no need to invoke a β phase separate from the α phase. Slowly
20 the β phase disappeared from the mainline metallurgical literature.
21
22
23
24
25
26
27
28
29

30 The following summarizes the demise of the β phase of iron from the metallurgical
31 literature.
32
33

- 34 • The 1917 Thum's *Practice Book in Elementary Metallurgy* refers to the β
35 modification of iron as the modification that exists between the α and γ
36 modification [14, p. 126].
37
- 38 • In 1923, Walter Rosenhain wrote in his *Metallurgy; an introduction to the*
39 *study of physical metallurgy*, that “ β (iron) is still the subject of discussion,
40 [15, p. 167].
41
42
- 43 • In 1930 Woldman's *Physical Metallurgy*, β is included in the Fe-C phase
44 diagram [16, Figure 21].
45
46
- 47 • In 1935, Doan's, *Principles of Physical Metallurgy* does not include the β
48 phase in the phase diagram but does include a horizontal line in the $\alpha + \gamma$
49 two phase region [17]².
50
51
52
53

54
55 ² This horizontal line is in the two phase region of the diagram between α (β) and γ phases. Above the horizontal
56 line the β phase is in equilibrium with γ , and below the horizontal line, α is in equilibrium with γ . See discussion.
57
58

- In 1936, Van Vliet's *Introduction to Physical Metallurgy* does not mention the β phase of iron [18].
- In 1940, Sachs' *Practical Metallurgy*, states that "the magnetic transformation which is completed (on heating) at the Curie point, ~ 1415 °F (770 °C) is not considered as a phase change, in spite of the marked changes in some of its physical properties" [19].

The reference books also show this trend. In the 1919 and 1925 editions of "*The Making, Shaping and Treating of Steel*", [20, 21] the β phase is shown in the phase diagram of Fe-C (Figure 197, 1925 4th edition), but in the discussion it is mentioned that since the two phases have "exactly the same space lattice" (eluding to the work of Westgren and Phragmén) they can not be different phases "without changing the definition of allotropy" [17, p. 661]. By the 5th edition [22] β is in the phase diagram with an attached "?" (Figure 340) and in the discussion the 1940 text reads "most careful investigators fail to note any difference in the properties of α and β iron *except in their magnetism*" (emphasis mine). No mention of β iron exists in the 1965 edition. Also the influential *Metals Handbook* [23], published by ASM makes no mention of β iron in the 1948 edition.

In 1939, Williams and Homerberg's *Principles of Metallography*, perhaps best sums up the thinking of mid 20th century metallurgists: "... if allotropy is defined as a change in crystal form, then β -iron, which would occur in the range from 906 °C to 768 °C, does not exist as an allotropic form" [24].

But is this really the case? Is the paramagnetic form of BCC iron really the same phase as the ferromagnetic form of iron? Clearly they have different physical properties. What about their structures? The careful work of Westgren and Phragmén did not show a difference, but could their x-ray diffraction experiment have shown a difference between a ferromagnetic structure and a paramagnetic one?

3. The Magnetic Symmetry of “BCC” Ferromagnetic iron

Let us consider the basic principles of crystal structure. We have all learned in our crystallography classes that crystal structure is *lattice plus a basis* (or motif). So we start with a BCC lattice, Fig. 3a. The lattice has the full cubic symmetry and can be represented as $Im\bar{3}m$. If we add to each lattice point a spherical atom, centered on the lattice points, the overall symmetry (space group) does not change, because the new symmetry is an intersection of the symmetry of the BCC lattice and the spherical symmetry of the atom. See Fig. 3b. This structure is called the BCC structure with the space group $Im\bar{3}m$. What happens however when we add an atom that has associated with it a magnetic moment, represented by a circulating electron? Clearly the symmetry has been lowered to that of $I\frac{4}{m}$, since only one of the orthogonal axes retains its four-fold rotation symmetry, that is the new structure is tetragonal. This latter structure is the structure which best represents a body centered unit cell with magnetic moments on or related to each lattice point. This shows that ferromagnetic α phase is NOT cubic, but rather tetragonal whilst the paramagnetic β phase is cubic since the magnetic vectors are randomly arrayed in a paramagnetic substance.

In the terms discussed above, α , β and γ are three allotropes of iron and should be represented as such on equilibrium phase diagrams. The difference between the ferromagnetic iron and paramagnetic iron is one of the ordering of the magnetic moments: in the cubic β phase, the moments are disordered: in the tetragonal α phase the moments are aligned and thus ordered. A material that changes its symmetry from cubic to tetragonal due to ordering undergoes a phase transformation.

The topic of magnetic symmetry is an interesting one and has been discussed in some of the text books of magnetism and crystal physics for the last fifty years or so [25-31]. See also [32, 33]

4. Some Effects of Magnetism on the Fe-C Phase Diagram

1
2
3 Consider the schematic phase diagram of Fe-C shown in Figure 4.
4

5 First we focus on the Curie temperature of pure iron, T_{Curie} . At this temperature the
6 low temperature ferromagnetic α iron phase has lost its magnetization, that is, the
7 phase has a zero magnetization and it is no longer ferromagnetic, but
8 paramagnetic. At and above the Curie temperature the stable phase is the
9 paramagnetic phase of BCC iron (β). This temperature is unlike the temperature
10 denoted β/γ where two phases may be in equilibrium with each other. Such
11 temperatures are equilibrium transition temperatures of first order structural
12 transitions which follow the Gibbs equilibrium phase rule. (The Gibbs phase rule
13 was derived assuming the transitions were first order transitions.) Since the Curie
14 temperature is not one where two phases coexist in equilibrium, it does not give
15 rise to a sharp rise in the heat capacity on heating, characteristic of first order
16 transitions. Rather, there is a gradual rise in the heat capacity which reaches a
17 maximum at the Curie temperature and subsequently decreases. There is no
18 concomitant release of thermal energy. This higher order phase transition occurs
19 because the loss of magnetization is continuous from below the transition
20 temperature.
21
22
23
24
25
26
27
28
29

30 The line in Fig.4 from the Curie temperature of pure iron to X, is displayed as dot-
31 dashed to show that it represents the Curie temperature of Fe-C alloys with $C\% <$
32 X in solution. The curve depicting the Curie temperature decreases slightly until it
33 intersects the BCC solubility curve. If an alloy of Fe-C with less than $X\%$ C were
34 to be heated to the temperature where it intersects the dot-dashed line, it would
35 transform from ferromagnetic iron to paramagnetic iron, there would be no thermal
36 arrest in the heating curve. Again this change of phase is not a first order
37 transition.
38
39
40
41
42
43

44 We now look at the horizontal line designated as XY. This line is horizontal since
45 it represents the Curie temperature of a specific Fe-C alloy, namely one with a
46 composition of X. It is drawn across the two phase field because any alloy of Fe-C
47 with compositions in that area will have the Curie temperature of the low
48 temperature a ferromagnetic phase as $T_C(X)$. This horizontal line is not a
49 designation of a three phase equilibrium line: it represents the Curie temperature of
50 the α phase which exists in equilibrium below it. It should be noted that below the
51 line, α (ferromagnetic iron) and γ are in equilibrium, while above the line, β
52 (paramagnetic, BCC) and γ (paramagnetic FCC) are in equilibrium.
53
54
55
56
57
58
59
60

1
2
3
4
5
6 Finally we look at the point Y in the diagram. The early representations of the
7 phase diagram of Fe-C showed a marked change of slope of the α/γ solubility
8 curve at this point. This was consistent with the phase diagram construction rules
9 for first order phase transitions. It was thought that since at that point the phase in
10 equilibrium with γ changed from α to β , the slope of the solvus must also change.
11 But the transition of α to β is a continuous one and since just below the
12 temperature T_X the α phase has nearly the same free energy as the β phase just
13 above T_X , the slope change here should be minimal. It should be noted that there
14 were never any data that were consistent with a change in slope at the point Y.
15
16
17

18
19 This in depth look at one region of a phase diagram that contains a ferromagnetic
20 to paramagnetic transition has shown that there are some details which must be
21 taken into account in the construction of such phase diagrams.
22
23
24
25

26 **5. Closing Thoughts**

27
28
29 In his influential monograph "Introduction to phase transformations in condensed
30 systems" Morris Fine says "... comparing the phases before and after
31 transformation, there are three basic types of transformation: (1) change in
32 structure, (2) change in composition, and (3) change in degree of order" [35]. The
33 ferromagnetic to paramagnetic transformation fits both conditions (1) and (3) of a
34 phase change.
35
36
37
38
39
40

41 **6. Summary**

42
43
44 The transformation of a ferromagnetic phase to a paramagnetic phase is a phase
45 transformation with changes in crystal symmetry. All such changes should be
46 denoted on phase diagrams and the different phases should be designated with
47 Greek letters and/or primes which show that they are not the same phase! Once
48 again [2] I urge that we bring the β phase back to Fe phase diagrams.
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 **Acknowledgements:** The author thanks his colleagues Prof. T. B. Massalski and
4 Prof. William A Soffa for constructive comments on an early draft of this paper.
5 He also thanks many comments over the years from his students on this topic.
6
7
8
9
10
11
12

13 **Note Added After Review:** A reviewer of this paper suggested that the δ phase be
14 renamed the β phase since it is the same phase. This author hesitates to agree with
15 this as δ has a long history of usage especially in describing microstructures
16 formed by the peritectic transformation. The proposal of this paper is to restore the
17 designation β to the paramagnetic BCC phase. I will leave it to others to argue
18 about renaming the δ phase to β !
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

References

1. C. E. Myers, The Enigmatic Polymorphism of Iron, *Journal of Chemical Education*, 1966, 43(6), p 303-306.
2. Thaddeus B. Massalski and David E. Laughlin, The Surprising Role of Magnetism on the Phase Stability of Fe (Ferro), *CALPHAD*, 2009, 33, p 3-7.
3. Morris Cohen and James M. Harris, The β - Iron Controversy, in Sorby Centennial Symposium, AIME , 1963, pp. 209-233.
4. F. Osmond and F. S. Werth, *Annales des Mines*, 8, 5, 1885
5. F. Osmond and F. S. Werth, *Memorial de l'Artillerie de la Marine*, 15, 225, 1885.
6. F. Osmond, *Memorial de l'Artillerie de la Marine*, 15, 225, 1885
7. F. Osmond, *Annales des Mines*, 17, 573, 1887.
8. F. Osmond, *J. Iron and Steel Institute*, 1, 38, 1890.
9. K. Honda, *J. of the Iron and Steel Institute*, 42, (II), p 190, 1915.
10. Gilbert N. Lewis and Merle Randall, *Thermodynamics and the free energy of chemical substances*, McGraw-Hill Book Company, New York, 1923.
11. J. W. Christian, *The Theory of Transformations in Metals and Alloys*, Pergamon Press, Oxford, 1965, page 1.
12. W. A. Soffa and D. E. Laughlin, *Diffusional Phase Transformations in the Solid State*, in *Physical Metallurgy*, Vol. I, edited by D. E. Laughlin and K. Hono, Elsevier, 851-1019, 2014
13. A. Westgren, G. Phragmén, X-ray studies on the crystal structure of steel, *J. Iron Steel Inst.* 1922, 1, vol 105, 241-273.

14. Ernest E. Thum , A Practice Book in Elementary Metallurgy, John Wiley & Sons, London 1917.
15. Walter Rosenhain, Metallurgy; an introduction to the study of physical metallurgy, London, Constable, second edition, 1923.
16. Norman Emme Woldman, Physical metallurgy; laboratory manual, New York, London, J. Wiley; 1930.
17. Gilbert Everett Doan , The principles of physical metallurgy, New York and London : McGraw-Hill Book Company, Inc., 1935.
18. Leland Russell Van Wert, An introduction to physical metallurgy, New York and London, McGraw-Hill, 1936.
19. George Sachs, Practical metallurgy; applied physical metallurgy and the industrial processing of ferrous and nonferrous metals and alloys, Cleveland, American society for metals, 1940.
20. J. M. Camp and C. B. Francis, editors, The making, shaping and treating of steel, Pittsburgh, Pa., Carnegie Steel Company 1919.
21. J. M. Camp and C. B. Francis, editors, The making, shaping and treating of steel, Pittsburgh, Pa., Carnegie Steel Company 1925.
22. J. M. Camp, editor, The making, shaping and treating of steel, Pittsburgh, Pa., Carnegie Steel Company 1940.
23. Metals Handbook, Taylor Lyman, Editor, The American Society from Metals, Cleveland, Ohio, 1948.
24. Robert S. Williams and Victor O Homerberg, Principles of Metallography, McGraw Hill 1939.
25. W. Opechowski, R. Guccione, Magnetic symmetry, in: Magnetism, vol. IIA, 1965, pp.105-165,
26. A.P. Cracknell, Magnetism in Crystalline Materials, Pergamon Press, 1975.

- 1
- 2
- 3 27. B.K. Vainshtein, Modern Crystallography I, Springer-Verlag, 1981.
- 4
- 5 28. S. Shaskolskaya, Fundamentals of Crystal Physics, Mir Publishers, Moscow,
- 6 1982, Chapter VIII.
- 7
- 8
- 9
- 10 29. L.A. Shuvalov, Modern Crystallography IV, Springer-Verlag, 1988.
- 11
- 12 30. S.J. Joshua, Symmetry Principles and Magnetic Symmetry in Solid State
- 13 Physics, Adam Hilger, Bristol, 1991.
- 14
- 15
- 16
- 17 31. L.D. Landau, E.M. Lifshitz, Statistical Physics, Pergamon Press, 1980.
- 18
- 19
- 20 32. D. E. Laughlin, M. A. Willard, and M. E. McHenry, Magnetic Ordering: Some
- 21 Structural Aspects, Phase Transformations and Evolution in Materials, , edited by
- 22 P.Turchi and A. Gonis, The Minerals, Metals and Materials Society, 2000, pages
- 23 121-137
- 24
- 25
- 26
- 27 33. Y. Shen and D.E. Laughlin, Magnetic effects on the symmetry of CBED
- 28 patterns of ferromagnetic PrCo₅, Phil. Mag. Lett. 62(3), 1990, 187-193.
- 29
- 30
- 31 34. Morris E. Fine, Introduction to phase transformations in condensed
- 32 systems. New York Macmillan, 1964.
- 33
- 34
- 35
- 36
- 37
- 38
- 39
- 40
- 41
- 42
- 43
- 44
- 45
- 46
- 47
- 48
- 49
- 50
- 51
- 52
- 53
- 54
- 55
- 56
- 57
- 58
- 59
- 60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

For Review Only

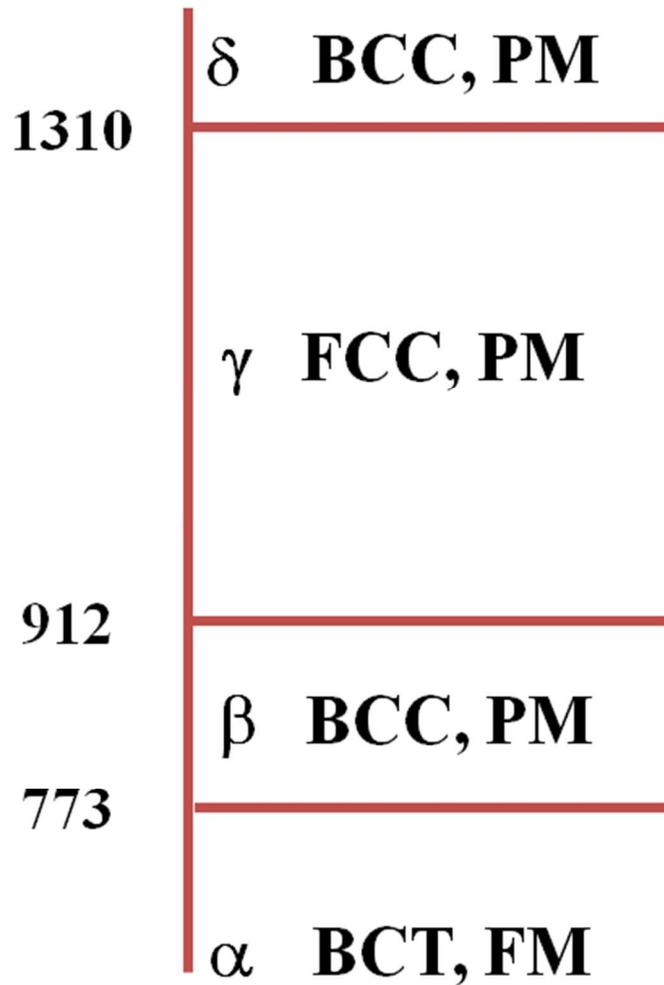


Figure 1. Temperature scale (in $^{\circ}\text{C}$) showing the regions of stability of the various Fe allotropes. PM = paramagnetic and FM = ferromagnetic.

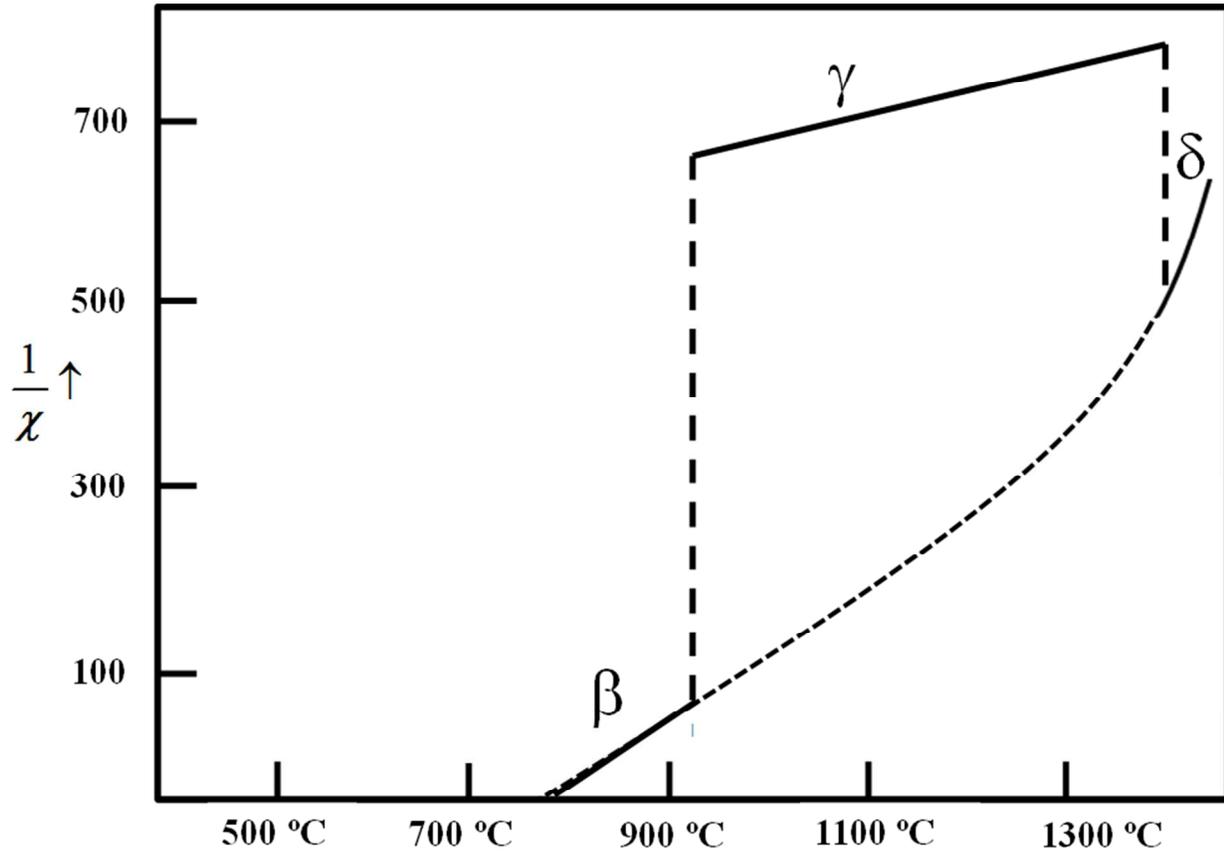


Figure 2. Inverse susceptibility of Fe as a function of temperature for the various phases. Note: below the Curie temperature the value the inverse susceptibility α is essentially zero. Also note that the β and δ phases can be seen to fall on a continuous curve, showing that they are the same BCC paramagnetic phase. After

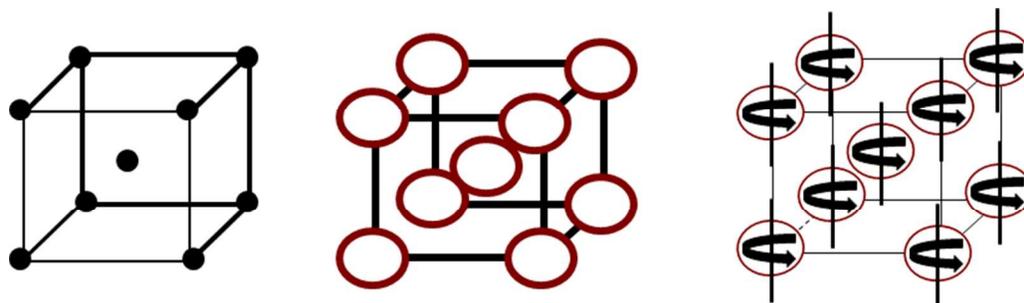


Figure 3. (a) A BCC Bravais lattice. (b) spherical atoms placed on the BCC Bravais lattice producing the BCC structure of the β and δ phases with the space group $Im\bar{3}m$ (c) Circulating arrows representing the magnetic spins present on the low temperature α phase. The symmetry of α is seen to be tetragonal, with space group $I\frac{4}{m}$.

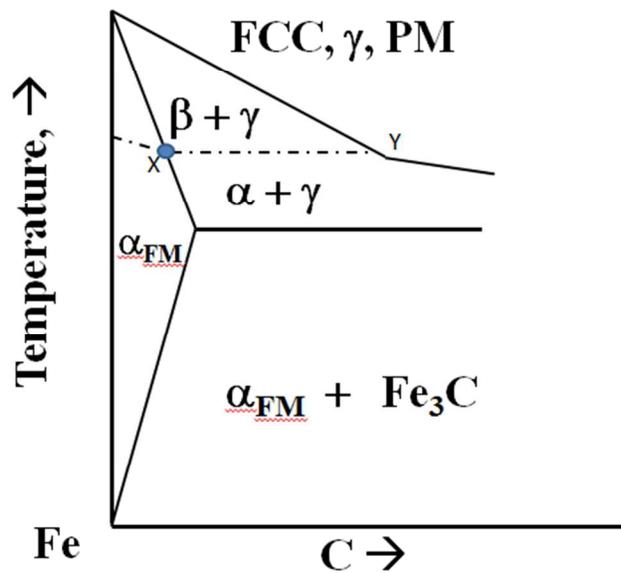


Figure 4. Schematic of the iron rich end of the Fe-C phase diagram. The dashed lines represent the Curie temperature of the alloy. The horizontal line is the Curie temperature of the alloy with the composition of the dot. The plot is exaggerated as the difference in the value of the Curie temperature of pure Fe and the of saturated C in Fe is less than one degree C.

The β – Iron Controversy Revisited

David E. Laughlin
ALCOA Professor of Physical Metallurgy
Carnegie Mellon University
Pittsburgh, PA USA

Abstract

Early twentieth century Fe-C phase diagrams designated the paramagnetic BCC iron phase (ferrite) as β iron. By the third decade of the last century this designation all but disappeared from the literature. Why was this? Should the β phase of iron be brought back to phase diagrams? What effects on the phase diagram would arise if we differentiate the ferromagnetic magnetic phase (α) from the paramagnetic phase (β)? In this paper I will discuss some of the history of this β iron controversy and discuss the effects on the Fe-C binary phase diagram. I will urge that β iron should be returned to iron phase diagrams so as to better represent a proper view of magnetic phase equilibria, magnetic symmetry and magnetic phase transformations.

1. Introduction

A glance at the Fe-C binary phase diagram reveals interesting and enigmatic features [1]. The low temperature iron rich phase is not a close packed structure which we are used to seeing in binary phase diagrams at low temperatures (either FCC or HCP) but rather is a phase usually designated as BCC α iron. Even more intriguing is the replacement of this BCC phase at 910 °C (1183K) by an FCC one (designated as γ iron) and the subsequent reappearance at 1391 °C (1664K) of the BCC phase at higher temperatures, designated as the δ phase. Another interesting feature is that in the modern phase diagrams the phases are labeled α , γ and δ (and ϵ if high pressures were included in the diagram) but no β phase? Why is this?

1
2
3 In an earlier paper Massalski and Laughlin [2] discussed the thermodynamic
4 reasons for the low temperature phase not being the FCC phase, and why the
5 paramagnetic BCC phase is replaced by the FCC one at higher temperatures. We
6 accounted for this interesting behavior in terms of the magnetic moments
7 associated with the Fe atoms, including the little known fact that at temperatures
8 below $\approx 70\text{K}$, metastable FCC γ iron becomes anti-ferromagnetic. The added
9 entropy due to the antiferromagnetic to paramagnetic transition at low
10 temperatures is what enables γ iron to replace the BCC phase at higher
11 temperatures. Massalski and Laughlin also discuss the “missing” β phase and
12 make a plea to reinstate it on the phase diagrams of iron based alloys.
13
14
15
16
17
18
19
20
21

22 In this paper, I will review some of the history of the β phase of iron and give the
23 stated reasons for its excising from the phase diagram. After criticizing the reasons
24 that have been given for its exclusion from the phase diagram, I will make a case
25 for reinstatement of the β phase to phase diagrams as the paramagnetic BCC phase
26 of iron. Some salient features of including the magnetic state of the phases on the
27 equilibrium Fe-C phase diagram will be discussed.
28
29
30
31
32
33
34

35 **2. Overview of the history of the β phase¹**

36
37 The α and β phases were named by Osmond and Werth in 1885 [4, 5]. In later
38 papers [6-8] Osmond reported on thermal arrest temperatures he called A_r (on
39 cooling) and A_c (on heating). The A_{r3} and A_{c3} temperatures correspond to the
40 critical temperatures on cooling and heating respectively of the transformation
41 between what we call today the FCC γ phase (paramagnetic) and the BCC
42 paramagnetic phase. The temperatures A_{r2} and A_{c2} (which were nearly identical)
43 correspond to the transformation of the BCC paramagnetic phase to the
44 ferromagnetic α phase, and vice versa. Today we call this temperature the Curie
45 temperature ($770\text{ }^\circ\text{C}$, 1043K), after Pierre Curie, (1859 – 1906).
46
47
48
49
50
51

52
53 ¹ I have gleaned many of the references in this section from the paper by Cohen and Harris, “The β -
54 Iron Controversy” [3].
55
56
57
58
59
60

1
2
3
4
5
6 Based on these results the phase diagrams of iron alloys in the early decades of the
7 20th century, the solid state phases of iron were delineated as
8

9 α , for the low temperature ferromagnetic phase,

10
11 β , for the BCC paramagnetic phase which forms from α at the Curie
12 temperature (A_{c2})
13

14
15 γ , the FCC paramagnetic phase which forms from β at ~ 910 °C (1183K), the
16 A_{c3} .
17
18

19
20 Later, the high temperature BCC phase which formed from the γ phase on heating
21 discovered by Honda [9] was called the δ phase. Thus the solid state phases of
22 iron were delineated as shown in Fig.1.
23
24
25
26
27

28 This delineation of the phases of iron implied that iron existed in three distinct
29 polymorphs or allotropes, namely those designated as the α , β and γ . It was
30 realized that the δ phase was a continuation of the β phase: both were BCC and
31 both were paramagnetic. In fact the plot shown in Fig. 2 of the inverse of the
32 magnetic susceptibility of Fe *versus* temperature shows that the susceptibility of
33 the δ phase is a continuation of that of the β phase. It also shows that at the A_{r2}
34 temperature (Curie temperature) the magnetic properties of β iron changed
35 discontinuously when it is cooled through the Curie temperature and that when β
36 iron transforms to α iron, the iron becomes a ferromagnetic phase.
37
38
39
40
41
42

43 So why was β extracted from the phase diagram? A little more than five decades
44 ago, Cohen and Harris [3] wrote an article entitled “The β – Iron Controversy”. In
45 a clear and concise fashion the authors reviewed the history of the β – Iron
46 “controversy”. They first discussed some of the properties which had been
47 attributed to β iron, such as its effect on hardness etc. After clearing up these
48 erroneous concepts (which the present paper does not discuss) they moved onto the
49 idea that α and β iron were different allotropes of iron, and made their opinion
50
51
52
53
54
55
56
57
58
59
60

1
2
3 clear: β should not be included in modern phase diagrams of iron and its alloys
4 because the “so-called α to β transition” is not a phase transition.
5
6

7 This statement has as its basic underlying assumption that the α and β states of Fe
8 are the same phase. This is said, even though the two states have very different
9 magnetic properties. This implies that properties of the states do not enter into the
10 definition of a phase. Now this is a strange approach as nearly all definitions of
11 thermodynamic phase includes the uniformity and specificity of physical and
12 chemical properties. As far back as 1923 in their highly influential text
13 “*Thermodynamics and the Free Energy of Chemical Substances*’, Lewis and
14 Randall [10] define a phase as:
15
16
17
18
19

20 a homogeneous region of matter in which its properties are the same or at
21 least vary continuously from point to point.
22
23

24 The same may be seen from Professor Christian’s rather complete description of a
25 phase:
26
27

28 “... an assembly of atoms or molecules which has attained equilibrium under
29 specified external constraints consists of one or more homogeneous and
30 physically distinct regions. The regions of each type may be distinguished by
31 a common set of parameters defining such intrinsic properties as density,
32 composition, etc. and they constitute a *phase* of the assembly. Two phases are
33 distinguishable if they represent different states of aggregation, different
34 structural arrangements in the solid, or have different compositions”[11].
35
36
37
38
39

40 More recently Soffa and Laughlin [12] define a phase as:
41
42

43 “.. a physically distinct homogeneous portion of a thermodynamic system
44 delineated in space by a bounding surface, called an interphase interface, and
45 distinguished by its state of aggregation (solid, liquid or gas), crystal
46 structure, composition and/or degree of order. Each phase in a material
47 system generally exhibits a characteristic set of physical, mechanical and
48 chemical properties and is, in principle, mechanically separable from the
49 whole.”
50
51
52
53
54
55
56
57
58
59
60

1
2
3 So on the basis of the drastic change in magnetic properties, the α to β
4 transformation should be designated as a phase change and thus α and β would be
5 different allotropes of iron.
6
7

8
9
10
11 It is at this point that the real problem seems to have raised its head. Allotropes are
12 said to have different crystal structures and α to β iron were thought to have the
13 *same crystal structure*, namely BCC. This was believed to have been shown by
14 some very careful high temperature x-ray diffraction of Westgren and Phragmén
15 reported in 1922 [13]. The x-ray patterns for the purported α and β phases (at 16
16 °C and 800 °C respectively) seemed to be identical except for the shift in spacing
17 due to thermal expansion. Since the crystal structures were the same the phases
18 were said to be the same. Thus, it was concluded there was no phase
19 transformation and no need to invoke a β phase separate from the α phase. Slowly
20 the β phase disappeared from the mainline metallurgical literature.
21
22
23
24
25
26
27
28
29

30 The following summarizes the demise of the β phase of iron from the metallurgical
31 literature.
32
33

- 34 • The 1917 Thum's *Practice Book in Elementary Metallurgy* refers to the β
35 modification of iron as the modification that exists between the α and γ
36 modification [14, p. 126].
- 37 • In 1923, Walter Rosenhain wrote in his *Metallurgy; an introduction to the*
38 *study of physical metallurgy*, that “ β (iron) is still the subject of discussion,
39 [15, p. 167].
- 40 • In 1930 Woldman's *Physical Metallurgy*, β is included in the Fe-C phase
41 diagram [16, Figure 21].
- 42 • In 1935, Doan's, *Principles of Physical Metallurgy* does not include the β
43 phase in the phase diagram but does include a horizontal line in the $\alpha + \gamma$
44 two phase region [17]².

54
55 ² This horizontal line is in the two phase region of the diagram between α (β) and γ phases. Above the horizontal
56 line the β phase is in equilibrium with γ , and below the horizontal line, α is in equilibrium with γ . See discussion.
57
58
59

- In 1936, Van Vliet's *Introduction to Physical Metallurgy* does not mention the β phase of iron [18].
- In 1940, Sachs' *Practical Metallurgy*, states that "the magnetic transformation which is completed (on heating) at the Curie point, ~ 1415 °F (770 °C) is not considered as a phase change, in spite of the marked changes in some of its physical properties" [19].

The reference books also show this trend. In the 1919 and 1925 editions of "*The Making, Shaping and Treating of Steel*", [20, 21] the β phase is shown in the phase diagram of Fe-C (Figure 197, 1925 4th edition), but in the discussion it is mentioned that since the two phases have "exactly the same space lattice" (eluding to the work of Westgren and Phragmén) they can not be different phases "without changing the definition of allotropy" [17, p. 661]. By the 5th edition [22] β is in the phase diagram with an attached "?" (Figure 340) and in the discussion the 1940 text reads "most careful investigators fail to note any difference in the properties of α and β iron *except in their magnetism*" (emphasis mine). No mention of β iron exists in the 1965 edition. Also the influential *Metals Handbook* [23], published by ASM makes no mention of β iron in the 1948 edition.

In 1939, Williams and Homerberg's *Principles of Metallography*, perhaps best sums up the thinking of mid 20th century metallurgists: "... if allotropy is defined as a change in crystal form, then β -iron, which would occur in the range from 906 °C to 768 °C, does not exist as an allotropic form" [24].

But is this really the case? Is the paramagnetic form of BCC iron really the same phase as the ferromagnetic form of iron? Clearly they have different physical properties. What about their structures? The careful work of Westgren and Phragmén did not show a difference, but could their x-ray diffraction experiment have shown a difference between a ferromagnetic structure and a paramagnetic one?

3. The Magnetic Symmetry of “BCC” Ferromagnetic iron

Let us consider the basic principles of crystal structure. We have all learned in our crystallography classes that crystal structure is *lattice plus a basis* (or motif). So we start with a BCC lattice, Fig. 3a. The lattice has the full cubic symmetry and can be represented as $Im\bar{3}m$. If we add to each lattice point a spherical atom, centered on the lattice points, the overall symmetry (space group) does not change, because the new symmetry is an intersection of the symmetry of the BCC lattice and the spherical symmetry of the atom. See Fig. 3b. This structure is called the BCC structure with the space group $Im\bar{3}m$. What happens however when we add an atom that has associated with it a magnetic moment, represented by a circulating electron? Clearly the symmetry has been lowered to that of $I\frac{4}{m}$, since only one of the orthogonal axes retains its four-fold rotation symmetry, that is the new structure is tetragonal. This latter structure is the structure which best represents a body centered unit cell with magnetic moments on or related to each lattice point. This shows that ferromagnetic α phase is NOT cubic, but rather tetragonal whilst the paramagnetic β phase is cubic since the magnetic vectors are randomly arrayed in a paramagnetic substance.

In the terms discussed above, α , β and γ are three allotropes of iron and should be represented as such on equilibrium phase diagrams. The difference between the ferromagnetic iron and paramagnetic iron is one of the ordering of the magnetic moments: in the cubic β phase, the moments are disordered: in the tetragonal α phase the moments are aligned and thus ordered. A material that changes its symmetry from cubic to tetragonal due to ordering undergoes a phase transformation.

The topic of magnetic symmetry is an interesting one and has been discussed in some of the text books of magnetism and crystal physics for the last fifty years or so [25-31]. See also [32, 33]

4. Some Effects of Magnetism on the Fe-C Phase Diagram

1
2
3 Consider the schematic phase diagram of Fe-C shown in Figure 4.
4

5 First we focus on the Curie temperature of pure iron, T_{Curie} . At this temperature the
6 low temperature ferromagnetic α iron phase has lost its magnetization, that is, the
7 phase has a zero magnetization and it is no longer ferromagnetic, but
8 paramagnetic. At and above the Curie temperature the stable phase is the
9 paramagnetic phase of BCC iron (β). This temperature is unlike the temperature
10 denoted β/γ where two phases may be in equilibrium with each other. Such
11 temperatures are equilibrium transition temperatures of first order structural
12 transitions which follow the Gibbs equilibrium phase rule. (The Gibbs phase rule
13 was derived assuming the transitions were first order transitions.) Since the Curie
14 temperature is not one where two phases coexist in equilibrium, it does not give
15 rise to a sharp rise in the heat capacity on heating, characteristic of first order
16 transitions. Rather, there is a gradual rise in the heat capacity which reaches a
17 maximum at the Curie temperature and subsequently decreases. There is no
18 concomitant release of thermal energy. This higher order phase transition occurs
19 because the loss of magnetization is continuous from below the transition
20 temperature.
21
22
23
24
25
26
27
28
29

30 The line in Fig.4 from the Curie temperature of pure iron to X, is displayed as dot-
31 dashed to show that it represents the Curie temperature of Fe-C alloys with $C\% <$
32 X in solution. The curve depicting the Curie temperature decreases slightly until it
33 intersects the BCC solubility curve. If an alloy of Fe-C with less than $X\%$ C were
34 to be heated to the temperature where it intersects the dot-dashed line, it would
35 transform from ferromagnetic iron to paramagnetic iron, there would be no thermal
36 arrest in the heating curve. Again this change of phase is not a first order
37 transition.
38
39
40
41
42
43

44 We now look at the horizontal line designated as XY. This line is horizontal since
45 it represents the Curie temperature of a specific Fe-C alloy, namely one with a
46 composition of X. It is drawn across the two phase field because any alloy of Fe-C
47 with compositions in that area will have the Curie temperature of the low
48 temperature a ferromagnetic phase as $T_C(X)$. This horizontal line is not a
49 designation of a three phase equilibrium line: it represents the Curie temperature of
50 the α phase which exists in equilibrium below it. It should be noted that below the
51 line, α (ferromagnetic iron) and γ are in equilibrium, while above the line, β
52 (paramagnetic, BCC) and γ (paramagnetic FCC) are in equilibrium.
53
54
55
56
57
58
59
60

1
2
3
4
5
6 Finally we look at the point Y in the diagram. The early representations of the
7 phase diagram of Fe-C showed a marked change of slope of the α/γ solubility
8 curve at this point. This was consistent with the phase diagram construction rules
9 for first order phase transitions. It was thought that since at that point the phase in
10 equilibrium with γ changed from α to β , the slope of the solvus must also change.
11 But the transition of α to β is a continuous one and since just below the
12 temperature T_X the α phase has nearly the same free energy as the β phase just
13 above T_X , the slope change here should be minimal. It should be noted that there
14 were never any data that were consistent with a change in slope at the point Y.
15
16
17

18
19 This in depth look at one region of a phase diagram that contains a ferromagnetic
20 to paramagnetic transition has shown that there are some details which must be
21 taken into account in the construction of such phase diagrams.
22
23
24
25

26 **5. Closing Thoughts**

27
28
29 In his influential monograph “Introduction to phase transformations in condensed
30 systems” Morris Fine says “... comparing the phases before and after
31 transformation, there are three basic types of transformation: (1) change in
32 structure, (2) change in composition, and (3) change in degree of order” [35]. The
33 ferromagnetic to paramagnetic transformation fits both conditions (1) and (3) of a
34 phase change.
35
36
37
38
39
40

41 **6. Summary**

42
43
44 The transformation of a ferromagnetic phase to a paramagnetic phase is a phase
45 transformation with changes in crystal symmetry. All such changes should be
46 denoted on phase diagrams and the different phases should be designated with
47 Greek letters and/or primes which show that they are not the same phase! Once
48 again [2] I urge that we bring the β phase back to Fe phase diagrams.
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 **Acknowledgements:** The author thanks his colleagues Prof. T. B. Massalski and
4 Prof. William A Soffa for constructive comments on an early draft of this paper.
5 He also thanks many comments over the years from his students on this topic.
6
7
8
9
10
11
12

13 **Note Added After Review:** A reviewer of this paper suggested that the δ phase be
14 renamed the β phase since it is the same phase. This author hesitates to agree with
15 this as δ has a long history of usage especially in describing microstructures
16 formed by the peritectic transformation. The proposal of this paper is to restore the
17 designation β to the paramagnetic BCC phase. I will leave it to others to argue
18 about renaming the δ phase to β !
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

References

1. C. E. Myers, The Enigmatic Polymorphism of Iron, *Journal of Chemical Education*, 1966, 43(6), p 303-306.
2. Thaddeus B. Massalski and David E. Laughlin, The Suprising Role of Magnetism on the Phase Stability of Fe (Ferro), *CALPHAD*, 2009, 33, p 3-7.
3. Morris Cohen and James M. Harris, The β - Iron Controversy, in Sorby Centennial Symposium, AIME , 1963, pp. 209-233.
4. F. Osmond and F. S. Werth, *Annales des Mines*, 8, 5, 1885
5. F. Osmond and F. S. Werth, *Memorial de l'Artillerie de la Marline*, 15, 225, 1885.
6. F. Osmond, *Memorial de l'Artillerie de la Marline*, 15, 225, 1885
7. F. Osmond, *Annales des Mines*, 17, 573, 1887.
8. F. Osmond, *J. Iron and Steel Institute*, 1, 38, 1890.
9. K. Honda, *J. of the Iron and Steel Institute*, 42, (II), p 190, 1915.
10. Gilbert N. Lewis and Merle Randall, *Thermodynamics and the free energy of chemical substances*, McGraw-Hill Book Company, New York, 1923.
11. J. W. Christian, *The Theory of Transformations in Metals and Alloys*, Pergamon Press, Oxford, 1965, page 1.
12. W. A. Soffa and D. E. Laughlin, *Diffusional Phase Transformations in the Solid State*, in *Physical Metallurgy*, Vol. I, edited by D. E. Laughlin and K. Hono, Elsevier, 851-1019, 2014
13. A. Westgren, G. Phragmén, X-ray studies on the crystal structure of steel, *J. Iron Steel Inst.* 1922, 1, vol 105, 241-273.

14. Ernest E. Thum , A Practice Book in Elementary Metallurgy, John Wiley & Sons, London 1917.
15. Walter Rosenhain, Metallurgy; an introduction to the study of physical metallurgy, London, Constable, second edition, 1923.
16. Norman Emme Woldman, Physical metallurgy; laboratory manual, New York, London, J. Wiley; 1930.
17. Gilbert Everett Doan , The principles of physical metallurgy, New York and London : McGraw-Hill Book Company, Inc., 1935.
18. Leland Russell Van Wert, An introduction to physical metallurgy, New York and London, McGraw-Hill, 1936.
19. George Sachs, Practical metallurgy; applied physical metallurgy and the industrial processing of ferrous and nonferrous metals and alloys, Cleveland, American society for metals, 1940.
20. J. M. Camp and C. B. Francis, editors, The making, shaping and treating of steel, Pittsburgh, Pa., Carnegie Steel Company 1919.
21. J. M. Camp and C. B. Francis, editors, The making, shaping and treating of steel, Pittsburgh, Pa., Carnegie Steel Company 1925.
22. J. M. Camp, editor, The making, shaping and treating of steel, Pittsburgh, Pa., Carnegie Steel Company 1940.
23. Metals Handbook, Taylor Lyman, Editor, The American Society from Metals, Cleveland, Ohio, 1948.
24. Robert S. Williams and Victor O Homerberg, Principles of Metallography, McGraw Hill 1939.
25. W. Opechowski, R. Guccione, Magnetic symmetry, in: Magnetism, vol. IIA, 1965, pp.105-165,
26. A.P. Cracknell, Magnetism in Crystalline Materials, Pergamon Press, 1975.

- 1
- 2
- 3 27. B.K. Vainshtein, Modern Crystallography I, Springer-Verlag, 1981.
- 4
- 5 28. S. Shaskolskaya, Fundamentals of Crystal Physics, Mir Publishers, Moscow,
- 6 1982, Chapter VIII.
- 7
- 8
- 9
- 10 29. L.A. Shuvalov, Modern Crystallography IV, Springer-Verlag, 1988.
- 11
- 12 30. S.J. Joshua, Symmetry Principles and Magnetic Symmetry in Solid State
- 13 Physics, Adam Hilger, Bristol, 1991.
- 14
- 15
- 16 31. L.D. Landau, E.M. Lifshitz, Statistical Physics, Pergamon Press, 1980.
- 17
- 18 32. D. E. Laughlin, M. A. Willard, and M. E. McHenry, Magnetic Ordering: Some
- 19 Structural Aspects, Phase Transformations and Evolution in Materials, , edited by
- 20 P.Turchi and A. Gonis, The Minerals, Metals and Materials Society, 2000, pages
- 21 121-137
- 22
- 23 33. Y. Shen and D.E. Laughlin, Magnetic effects on the symmetry of CBED
- 24 patterns of ferromagnetic PrCo₅, Phil. Mag. Lett. 62(3), 1990, 187-193.
- 25
- 26
- 27 34. Morris E. Fine, Introduction to phase transformations in condensed
- 28 systems. New York Macmillan, 1964.
- 29
- 30
- 31
- 32
- 33
- 34
- 35
- 36
- 37
- 38
- 39
- 40
- 41
- 42
- 43
- 44
- 45
- 46
- 47
- 48
- 49
- 50
- 51
- 52
- 53
- 54
- 55
- 56
- 57
- 58
- 59
- 60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

For Review Only