The surprising role of magnetism on the phase stability of Fe (Ferro)

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A B S T R A C T

We discuss the phase stability of the important element Fe in terms of the contributions to stability from the various forms of magnetism that exist in Fe. We point out that the ferromagnetic Fe is not cubic and that it is reasonable to return the beta phase of Fe to the phase diagrams based on Fe to designate paramagnetic BCC form of iron. We give a working definition of a phase, which includes the term "order parameter" following the insights of Landau.

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1. Introduction

The phase stability of many elements shows the following pattern:

1. A low enthalpy is mainly responsible for the choice of structure at low temperatures.
2. At higher temperatures, structures (phases) are stable which have higher entropies.

This often translates into the low temperature phase being a close packed one and the high temperature phase having a more open structure, that is, a less close packed structure. For example, the low temperature phase of Ti is close packed hexagonal (HCP) while the high temperature phase is BCC.

Fe does not follow this pattern. In fact, there are several interesting aspects of the phase stability of Fe which is the topic of this paper.

2. Facts about the stability of Fe

1. The BCC phase, denoted as α, is the low temperature phase of Fe.

2. This BCC Fe phase transforms on heating to the FCC γ phase at about 910 °C.
3. The FCC γ phase transforms on heating to the BCC δ phase at about 1400 °C.

Another interesting fact is that although in the earlier literature there used to be a phase designated as β, currently the recognized sequence is α, γ and δ.

In this paper we discuss these temperature ranges of the stability of Fe phases and comment on them in terms of the additional influence of the magnetic transitions on the thermodynamics of Fe.

3. Discussion of the facts about the stability of Fe[1]

The allotropic transformations in Fe are interesting examples of important contributions to structural stability from magnetic effects that can bring about phase changes in a unary system. The temperature/pressure phase diagram for Fe, shown in Fig. 1, displays the "facts" listed above. The overall transformation sequence on heating at ambient pressure is summarized as:

$$\alpha \to \gamma \to \delta \to \text{liquid}.$$

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[1] See also *Constitution and magnetism of Fe and its alloys*, Werner Pepperhoff and Mehmet Acet. Berlin [2] for a detailed discussion of the influence of magnetic effects on the phase stability of Fe.
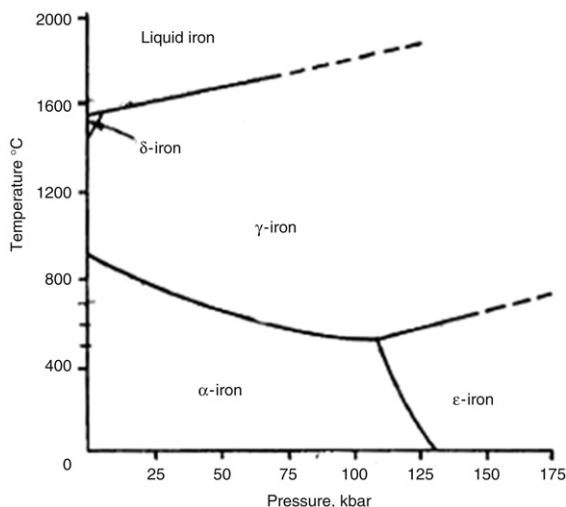
Fig. 1. The temperature/pressure phase diagram for Fe [1].

Application of pressure changes the temperatures of these transitions (which can be calculated using the Clapeyron equation). A substantial pressure also makes possible another structure modification, to the HCP ε-form of Fe, above approximately ~125 kbar.

The trends with temperature at ambient pressure of the volumes per atom (Ω) and the closest interatomic distances of approach (d) in each structure are shown in Fig. 2 [1]. The Ω values of BCC are larger than those of FCC. Hence, the BCC structure can be regarded as more "open" and it allows for more vibrational choices, making the vibrational entropy S_{vib}^{bcc} larger than S_{vib}^{fcc}. This feature makes the negative TS term in the Gibbs energy of the BCC phase to increase more rapidly with temperature than in the FCC phase. The 12 atoms in the FCC structure are slightly farther apart than the eight nearest atoms in the BCC (d_{bcc}) which are closer ($d_{bcc} < d_{fcc}$), but the distance between the next 6 atoms in the BCC structure exceeds the closest distance of approach d_{bcc}. It is for this overall reason that the BCC structure is regarded as less close-packed compared with the FCC structure. The fact that volume per atom differences between the two structures are quite small indicates that their total energies are similar, and confirms that the bonding between atoms in the two different crystal structures of Fe is essentially metallic.

We now turn to the facts about the phases listed above and ask the obvious questions:

1. Why is the BCC form of Fe stable at low temperatures? Usually, a close packed allotrope (such as FCC or HCP) is stable at low temperatures because enthalpy is generally lowered by close-packing, and entropy is less important.
2. Why does the BCC phase transform to the close-packed FCC phase on heating? Once again this seems backwards because, in general, on heating a more open structure, which therefore has higher vibrational entropy, should be the more stable phase. Typically, more open structures are observed in most elements at higher temperatures.
3. Why does the FCC γ revert to the BCC δ at even higher temperatures? Is the large vibrational entropy of the BCC δ the only factor involved in this transformation?

Finally, we may ask, why in the current literature there is no β phase included in the transformation sequence?

To answer the phase stability questions we must look at the specific heats of the phases in question, shown below in Fig. 3.

The transformation at 1184 K (910 °C) on heating, from α to γ is a clear example of a first order phase transformation in that at the
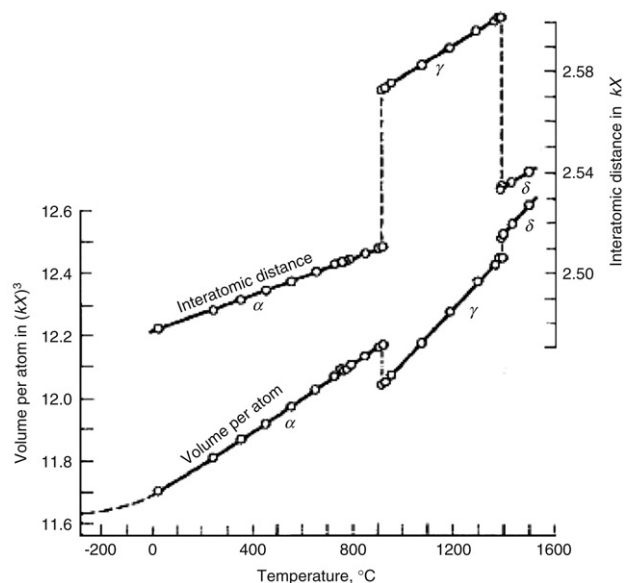

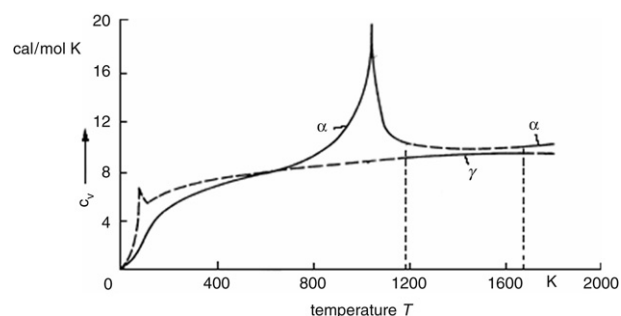**Fig. 2.** Temperature dependence of lattice parameters and the volume per atom in α and γ Fe. See footnote 1.

Fig. 3. Schematic specific heat (C_V) versus temperature curves for the α and γ phases of Fe. Partially based on Haasen [2] (for the purpose of the discussion which follows, there is very little difference between C_V and C_p and the symbol C_p will be used throughout the reminder of this paper).

transformation temperature both phases are present and there is a distinct discontinuity of specific heat, giving rise to a latent heat of transformation. The same is true of the transformation from γ to δ at 1665 K (1392 °C). However, there are two interesting portions of the specific heat curves, namely the peak which appears at about 50 K for the γ phase and another peak at 1042 K for the α phase. These peaks are due to the need to increase the energy supplied to the material to continue to heat it up. They are related to the fact that the ordered spins of the *antiferromagnetic* FCC γ Fe and of the *ferromagnetic* BCC α Fe must be randomized to change these phases into their respective paramagnetic states.

The transition temperature of the *antiferromagnetic* FCC γ Fe to the *paramagnetic* FCC γ Fe is called the Néel temperature, T_N. In *antiferromagnetically* (AF) ordered materials, the magnetic spins are aligned in opposite directions with respect to neighboring spins, and thus can be considered as being ordered. This has been demonstrated to occur in micron-size metastable γ-Fe particles embedded in Cu, which remain FCC on cooling [3]. In an *antiferromagnetic* arrangement the opposite magnetic moments cancel one another and hence the overall magnetization is equal to zero. However, this *antiferromagnetic* arrangement contributes to the structural energy, and heat is needed to randomize magnetic moments. The transition is indicated by the small peak in the C_P curve for the γ-phase in Fig. 3. This figure shows the C_P trends for both the FCC and BCC Fe phases, with some extrapolations into

metastable regions (shown by dashed lines), which seem quite reasonable. Both magnetic states stabilize the respective crystal structures at low temperatures.

Question 1 can now be addressed as follows. At 0 K, the ferromagnetic ordering in the BCC α phase causes the internal energy (and enthalpy) of that phase to be lower than the internal energy (and enthalpy) of the *antiferromagnetic* (and *paramagnetic*) FCC phase, i.e. $H_\alpha(FM) < H_\gamma$. This is so because the large exchange energy of the aligned magnetic moments of the *ferromagnetic* BCC Fe greatly reduces its internal energy. Thus, even though the *ferromagnetic* BCC Fe is less close-packed than FCC γ, it is the equilibrium phase at low temperatures [4].

The answers to questions 2 and 3 are more complex and involve the influence of entropy, as well as internal energy. To answer them we need to consider in more detail the behavior of the specific heats with temperature for the α and γ phases (see Fig. 3). Both C_p curves show a peak corresponding to a magnetic transition. We consider two aspects of the entropy of the α and γ phases, namely their *vibrational entropy* and their *magnetic spin entropy*. As mentioned earlier, the *vibrational entropy* usually is larger for BCC structures than for FCC structures. This is the reason why BCC structures are usually more stable than FCC ones at higher temperatures. In the case of Fe, however, we must also take into account the entropy due to the disordering of the spins.

At low temperatures, the *antiferromagnetic* to *paramagnetic* transition in γ Fe increases its configurational spin entropy to the extent that the overall entropy for the close packed γ phase becomes greater than that of the more loosely packed *ferromagnetic* α phase. This excess entropy (due to the disordering of the magnetic spins at the Neel temperature) is the cause of the appearance of the γ phase at higher temperatures, as can be seen from the equation for the Gibbs energy of the γ phase:

$$G^\gamma = H_o^\gamma + \int_0^T C_p^\gamma \, dT - T \int_0^T \frac{C_p^\gamma \, dT}{T}.$$

It is the negative TS term that eventually causes the γ phase to have a lower Gibbs Energy at higher temperatures, because it continues to decrease as the temperature increases. Hence the FCC phase replaces the BCC one at about 910 °C; that is, the α to γ structural transformations occurs. This BCC to FCC transformation on heating is opposite to the more usual FCC to BCC one, because, in the case of Fe, it is the entropy due to the spin disordering that determines the equilibrium phase, not the lattice vibrational entropy term.

The graphic illustration of these transformations is shown in Fig. 4. At 910 °C the G_γ curve crosses the G_α curve, producing a change of phase from BCC to FCC. However, on further heating the excess specific heat of the α phase in the Curie temperature range makes the negative TS term of the α important and, as a result, the G_α curve re-crosses the G_γ at $\sim$1400 °C. Thus, the large entropy due to the randomizing of the magnetic spins in the α phase in concert with its larger vibrational entropy allows the BCC phase to appear again, this time being labeled as the δ phase.

The importance of magnetic effects in Fe can be summarized as follows:

1. If γ Fe were not *antiferromagnetic* at the very low temperatures, γ Fe would never be stable enough to form as the higher temperature phase because the *ferromagnetic* BCC form has lower enthalpy and the *paramagnetic* BCC form has higher entropy. The antiferromagnetic state of the γ phase at very low temperatures contributes to its specific heat peak during magnetic randomization in the range of the Neel temperature during heating and this situation is sufficient to subsequently lower the free energy of the FCC phase below that of the BCC phase at 910 °C.
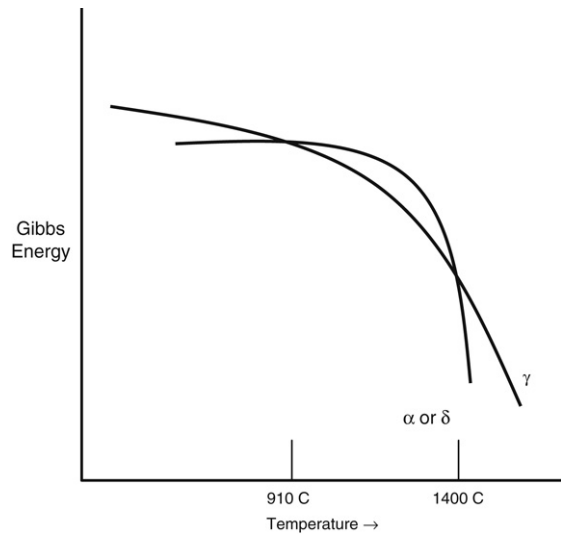

Fig. 4. A schematic of the Gibbs free energy of the BCC (α and δ) and the FCC (γ) phases in Fe.

2. If the Neel transition temperature in γ Fe were a little higher, than that shown in Fig. 3, the FCC (γ) Fe would most likely never become stable-enough to compete with the α phase. This is because the γ phase free energy would not have a sufficiently large negative TS entropy term, resulting from the integration of its specific heat curve over temperature, to lower the free energy of γ sufficiently to make it stable with respect to the α above 910 °C. In terms of Fig. 4, the Gibbs free energy curve for γ Fe would continue to lie above that for α/δ.

3. Similarly, if the Curie transition temperature of the *ferromagnetic* to *paramagnetic* transition in the α phase were a little lower in temperature, the large negative TS term (again resulting from the integration of the specific heat curve over temperature) would tend to twist the BCC α/δ free energy curve downwards with rising temperatures sooner and stabilize the α phase relative to that of the γ phase at all temperatures. Thus, again, the FCC (γ) Fe might never form at elevated temperatures.

Clearly, without the magnetic effects (including their particular critical respective magnitudes and the critical corresponding disordering temperatures), there would be no FCC γ phase in pure Fe.

As is well known, all sorts of phase transformations occur in the alloys of iron. Each alloying addition alters not only the respective positions of the Neel and Curie temperatures in the diagrams like that in Fig. 3, but also the magnitudes of the specific heat peaks themselves. In turn, both the respective positions and the forms of the two Gibbs free energy curves, like those in Fig. 4, hold the answers to the resulting phase diagrams. In metallurgical terms, the "γ loop" either tends to widen, or to shrink and close in the respective alloy phase diagram. As a result, the alloys of iron constitute a fascinating field of diverse phase transformation and heat treatment opportunities. The magnetic interactions clearly play a key role in this. A modeling of the positions of the Neel and Curie temperatures and of the magnitudes of the specific heats associated with the respective antiferromagnetic and ferromagnetic to paramagnetic transitions would provide an interesting opportunity to quantify some of the resulting thermodynamic parameters.

4. What about the β phase of Fe?

The last question remains to be answered, namely why is there no β phase in the Fe phase diagrams.

Actually, a β phase was denoted in phase diagrams based on Fe at the turn of the 19th to 20th century; it was however removed in later publications. One of the reasons for its removal was that for many years in the metallurgical community, the transformation from ferromagnetic to paramagnetic Fe was not thought to be a phase transformation at all! This confusion amongst metallurgists arose from an incomplete understanding of the symmetry of the structure of the magnetic phases as well as from a narrow definition of a phase.

Thus, although there was evidence of property changes (such as electrical resistivity, or specific heats etc.) occurring over a range of temperatures in the region of the magnetic transition, the transition was not considered to be a phase change because no change in structure was detected [5]. If both the ferromagnetic and paramagnetic phases have the same structure, they were thought to be the same phase. Hence the designation β (which was the symbol for the paramagnetic BCC Fe) was dropped. To this day both the *paramagnetic* and *ferromagnetic* states of BCC Fe are designated by the same Greek letter, α.

But are the *paramagnetic* and *ferromagnetic* states of BCC Fe the same phase? Typical definitions of a phase from commonly used textbooks are;

1. "A *phase* can be defined as a portion of the system whose properties and composition are homogeneous and which is physically distinct from other parts of the system …" [6].
2. "…the equilibrium state …contains regions which exhibit the same properties, such as specific volume, composition, and structure. These regions constitute a phase" [7].
3. "A phase is defined as a structurally homogeneous portion of matter characterized by the same intensive properties. A phase is thus a uniform composition and its intensive properties are constant" [8].
4. "An assembly of atoms or molecules which has attained equilibrium under specified external constraints consists of one or more homogeneous and physically distinct regions. The regions of each type may be distinguished by a common set of parameters defining such intrinsic properties as density, composition, etc. and they constitute a *phase* of the assembly. Two phases are distinguishable if they represent different states of aggregation, different structural arrangements in the solid, or have different compositions [9].

If we accept these definitions, they alone, imply that that *paramagnetic* to *ferromagnetic* "change" is indeed a phase change, since a *paramagnetic* phase has different magnetic properties than a *ferromagnetic* phase. However, because a phase was said to have a distinct "structure" a problem arose. As far as could be determined by x-ray diffraction, the structure of *ferromagnetic* Fe was the same as that of *paramagnetic* Fe [5]. Thus, no change of phase was thought to have occurred when Fe lost its magnetism at the Curie temperature range.

However, in the $\alpha \rightarrow \beta$ transition, a symmetry change, and hence a change in structure, must accompany the magnetic change. Since the magnetic spins are aligned along the [001] direction of Fe within a ferromagnetic domain, the symmetry of ferromagnetic Fe is actually tetragonal, with a space group I4/m [10–15]. That this is so can be seen from the fact that the [100] and [010] directions are not equivalent to the [001] direction along which the magnetization lies. The ferromagnetic to paramagnetic change which occurs on heating takes place by what is known as a *higher order transition*. Changes in properties such as specific heat occur over a range of temperatures as can be seen from the large peak in the specific heat curve for α-Fe corresponding to the magnetic disordering in Fig. 3. The temperature associated with this change of phase is called the Curie temperature, T_{Curie}. Its value for pure Fe is approximately 1042 K (769 °C). Thus, this change in magnetic

state occurs with a change in symmetry and hence a change in structure. This is so by all the above definitions of a phase change.

The definitions listed above are not complete, in that no explicit mention of order parameter is included, though that of Christian [9] does use the phrase "common set of parameters". The order parameter is a concept that was developed by Landau in the 1930s [16]. Including it, we suggest the following definition of a phase:

A **phase** is a physically distinct region of a system which has attained thermodynamic equilibrium, and which has a specific set of order parameters ($\eta_1, \eta_2, \ldots$) which specify its physical properties. Such parameters include composition, structure, atomic order, magnetic order, ferroelectric order, etc.

Therefore, a **change of phase** occurs when one or more of its order parameters changes discontinuously from one value to another or from zero to a non-zero value (or vice versa).

Thus, when a *ferromagnetic* phase changes to a *paramagnetic* phase, a phase change has occurred, since the magnetic order parameter, the magnetization of the material, changes from a non-zero value to zero on passing through the Curie temperature on heating. There really is a β Fe phase, which is the paramagnetic BCC α!

5. Summary

We have discussed the phase stability of the important element Fe. We have shown that it is necessary to include the various forms of magnetism that exist in Fe to fully elucidate its stability. Along the way we pointed out that ferromagnetic Fe is not cubic and that it is reasonable to return the β Fe phase to the phase diagrams of Fe to designate *paramagnetic* BCC Fe. We also give a working definition of a phase, which includes the term "order parameter" following the insights of Landau.

Note added in proof

After submitting the final version of this paper we discovered a paper by Qing Chen and Bo Sundman entitled "*Modeling of Thermodynamic Properties for Bcc, Fcc, Liquid, and Amorphous Iron*" in the *Journal of Phase Equilibria* Vol. **22** No. 6 pp. 631–644 (2001), which deals quantitatively with some of the aspects with which we deal qualitatively in our paper.

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