COMMEMORATIVE LECTURE BY THE FIFTY-FIFTH GOLD MEDALIST OF THE JAPAN INSTITUTE OF METALS

Comments Concerning Some Features of Phase Diagrams and Phase Transformations*

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Several interesting features in the study of stabilities of phases, and in phase transformations, are discussed. It is proposed that symmetry considerations related to the presence of magnetism in iron suggests that the respective phases, BCC alpha and FCC gamma, have in fact lower symmetries than cubic. A proposal is made that the symbol beta used in the past for the designation of the paramagnetic BCC iron should perhaps be returned as a feature in phase diagrams. It is proposed that since the thermal activation is a major feature in the behavior of isothermal martensites, a more suitable designation for these types of phase transformations might be ''thermally activated martensites'', or TAMs. Massive transformations are discussed briefly and it is emphasized that they present a specific example of an idiomorphic transformation process, not requiring the need for orientation relationships (ORs) between the parent and product phases.

1. Phase Diagrams and Phase Stability

1.1 Symmetry and the structure of phases–Should we return the β phase to the Fe phase diagram?

In terms of conventional crystallography, the structure of a phase may be defined as a result of positioning of a ''motif'' of atoms (or groups of atoms) upon a ''lattice'' of points in space. Difficulties arise when we begin to apply this concept to motifs that are more complicated than just neutral single atoms. I will illustrate this with reference to the elements iron (Fe) and plutonium (Pu), which exhibit allotropic structure changes depending on temperature. The sequence of allotropic phases in Fe includes the phase β, as was considered to be the case in the late 1800's and early 1900's. This was based mainly upon the work of Roberts–Austen(1), but was put into question later by many authors(2)–(4) when the structures of the α, β and δ phases were determined by X–ray diffraction to be all BCC(5).

The difference between the α and β phases involves the change in magnetism: α phase is ferromagnetic below the Curie temperature, and β phase is paramagnetic above. In the late 1920's and 1930's the β phase was abandoned in published phase diagrams mainly because X–ray diffraction seemed unable to reveal any change of structure. However, one may correctly argue that there is a change of symmetry, from tetragonal to cubic, and that this constitutes a phase change. Recently, D.E. Laughlin and I have argued this point in a contribution to the Ricardo Ferro Symposium(6). We proposed to adopt a definition of a phase that includes order parameters specifying additional properties to be considered in addition to the composition and structure; such parameters as atomic order, magnetic order, electronic configuration, etc. This enlarged definition of a phase can already be found earlier in the writings of Landau(7), or Christian(8), and others.

As illustrated in **Fig. 1**, the overall symmetry is lowered when the motif of ordered magnetic moments is included. The repetition of lattice (points) and the motif of the atoms with aligned magnetic moments reduce a plane group symmetry of *4mm* to a plane group symmetry of *2mm* only by a change in the motif, not the lattice. As a consequence, if all such moments are aligned in one direction on a bcc lattice, say along the [001] direction, they create an overall directional motif that changes the structure. Some people would say that even if the cubic lattice retains the symmetry of the crystal parameters ($a=b=c$), the total spatial symmetry of

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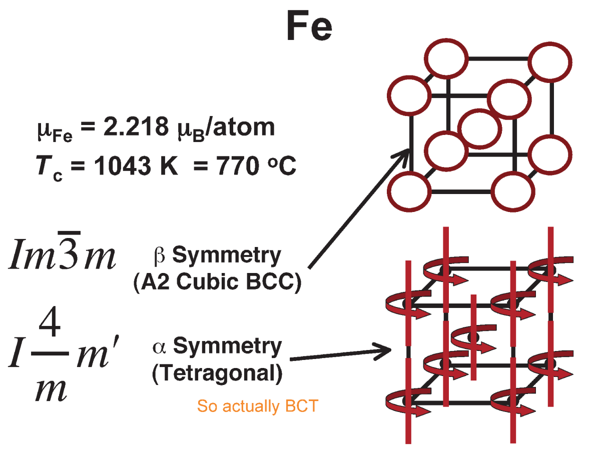

Fig. 1 The BCC crystal structure, including magnetic and symmetry information(9).

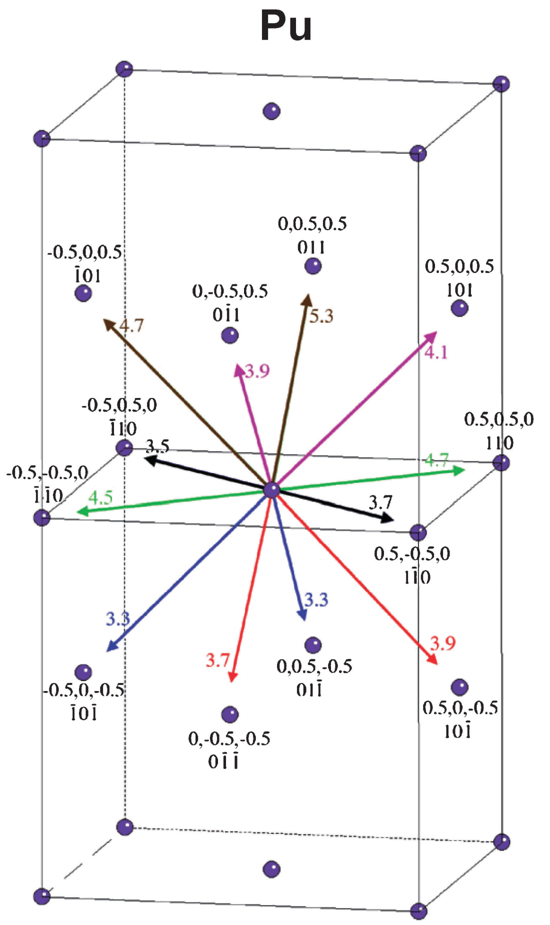

Fig. 2 Two stacked fcc unit cells with the central atom showing the 12 nearest neighbours. In the case of plutonium, the 12 bonds with the nearest neighbours widely vary with strength and can be separated into six pairs: blue (3.3), black (3.5–3.7), red (3.7–3.9), pink (3.9–4.1), green (4.5–4.7) and brown (4.7–5.3). When the fcc lattice is combined with the motif of these bond strengths, the resultant space group is monoclinic Cm(14).

the structure is nevertheless lowered from $Im\bar{3}m$ to $I\frac{4}{m}m'$, due to the aligned moments. Arguments of this kind have been used for several years now by Laughlin *et al.*(9) and others(10) to discuss the symmetry of crystals that have magnetic moments associated with the atoms. So, the motif can change the lattice. That is a tricky statement, but there are plenty of comments on this now in the literature. Some people may say, I will accept this concept if the presence of the BCT structure is demonstrated experimentally, even if it cannot be demonstrated by X–ray diffraction. Perhaps measurements of magnetostriction can accomplish this(11). Numerous features of magnetic materials, such as magnetic domains, domain interactions, magnetocrystaline anisotropy, and magnetostriction, can be addressed more accurately by starting with the full symmetry aspects of the magnetic state, i.e. the structure with reduced symmetry due to the magnetic ordering rather than the original cubic lattice. Electronic structure calculations for such materials produce more consistent results when the symmetry is reduced due to the ordered magnetic state. Accurate orbital magnetic moments of BCC iron can only be obtained from calculations that introduce a lowering of the symmetry, from 48 (cubic) to 16 (tetragonal) operations, resulting from the preferred orientation of the magnetic spin moments along the [001] easy axis. Cubic symmetry does not support ferromagnetism because the aligned moments always favor a special direction. So, as more "ground state" calculations are becoming involved in assessment of phase stability, perhaps the time has come to accept these subtle features of crystal structure.

Although not cubic, $PrCo_5$ has yielded experimental evidence of symmetry reduction upon magnetic ordering. Shen and Laughlin(12) have shown by convergent beam electron diffraction that the projected point group symmetry along the [0001] direction of $PrCo_5$ is reduced from *6mm* to *6* on magnetic ordering. This implies that the space group changes from $P6/mmm$ in the paramagnetic state to $P6/mm'm'$ in the ferromagnetic state. Equally interesting are the calculations by Widom and Mihalkovic(13), regarding the crystal structure of boron. Experimental work suggests that the β–rhombohedral (black) form is stable over all temperatures from 0 K to melting. However, early calculations indicate that its energy is larger than the energy of the α–rhombohedral (red) form, implying that the β phase cannot be stable at low temperatures. Furthermore, the β form exhibits partially occupied sites, seemingly in conflict with the thermodynamic requirement that entropy vanishes at the low temperatures (the Third Law). Using electronic density functional methods, Widom and Mihalkovic conclude that this unique, energy–

minimizing pattern of occupied and vacant sites can be stable at low temperatures, but this seems to break the β–rhombohedral symmetry.

Returning to the general question regarding the sequence of phases in Fe, as depicted at present in phase diagrams and accepted in books(2)–(4), should we restore the β symbol to the phase diagram? My personal preference is yes, but perhaps another solution would be to call the present α phase as α', and the phase above the Curie temperature as α, similarly to the situation with the atomic order transition (β' to β) in the case of the Cu–Zn β brass.

Later on I shall remind you that at very low temperatures the (metastable) FCC gamma phase of Fe may also be regarded as tetragonal. When gamma becomes antiferromagnetic (AF) below the Neel temperature (T_N), gamma AF may in fact be regarded as no longer cubic, but FCT in this new phase nomenclature context. One can ask–is the ferromagnetic FCC Ni also actually FCT? Laughlin suggests that it is actually rhombohedral, because the magnetic moments are aligned in the [111] direction.

Perhaps I should also mention that in the case of other elements that exhibit numerous allotropic changes, there are similar arguments about symmetry, namely, that the acceptance of the existence of additional "order parameters" (magnetic, electronic, etc.) affecting the motif in the definition of a "phase" tends to reduce the crystal structure symmetry. We can start with a "cubic lattice", but if we add to it a motif (for example a non–symmetric distribution of the electronic bonding forces which show directional features) the resulting "structure" can be regarded as having a "lower symmetry". For example, in Pu the sequence of phases is $\alpha \rightarrow \beta \rightarrow \gamma \rightarrow \delta \rightarrow \delta' \rightarrow \varepsilon \rightarrow$liquid. The X–ray studies show that the δ structure is FCC. It can be argued, however(14), that Pu atoms in the Pu δ phase are not all electronically the same, and may exhibit "lattice position dependence" indicated by the fact that the calculated bonding forces between them vary strikingly and are highly unisotropic, depending on the location on the FCC lattice. There is still an additional difficulty here, namely the fact that first principles calculations are "ground state" calculations (at 0 K) and the actual δ structure exists at much higher temperatures.

The picture of bonding forces between atoms in Pu, as illustrated in **Fig. 2**, suggests that Pu is totally different from a classical FCC metal, like Al, where all forces between atoms are the same(14), and where the structure is indisputably A2. So, here again, the total symmetry of the Pu δ phase may be considered to be reduced from FCC to c–centered monoclinic, if the arguments based on the first principles calculations for 0 K are accepted.

1.2 Competition for stability between the allotropic phases in Fe: –Is the occurrence of antiferromagnetism at very low temperatures in the gamma phase of Fe responsible for the observed BCC > FCC > BCC transition?

As is well known, the role of magnetism in deciding the competition for stability between the observed allotropic changes with temperature in Fe can be considered in terms of the usual thermodynamic Gibbs free energies:

$$G^i = H^i - TS^i \tag{1}$$

where i refers to either phase α or phase γ. Similarly, both enthalpy and entropy are expressed as

$$H^i = H_0^i + \int_{T_0}^{T} C_P^i dT \tag{2}$$

and

$$S^i = S_0^i + \int_{T_0}^{T} \frac{C_P^i}{T} dT, \tag{3}$$

where C_P^i represents the specific heat at constant pressure for the phase i, T_0 is 0 K and H_0^i is the enthalpy at 0 K. Thus, eq. (1) is explicitly rewritten as

$$G^i = H_0^i + \int_{T_0}^{T} C_P^i dT - T \int_{T_0}^{T} \frac{C_P^i}{T} dT. \tag{4}$$

Keeping in mind the Third Law(15), the entropy S_0 of a pure element is zero at 0 K. Thus, we see that the Gibbs free energy can be expressed in terms of the specific heats C_P, which can be measured experimentally, or evaluated from a suitable model(16)(18)(19):

$$C_P = 3R\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/\mathrm{T}}}{(e^{\Theta_E/\mathrm{T}} - 1)^2} + aT + bT^4 + C_P^{mag}, \tag{5}$$

where the first term represents the Einstein specific heat with the Einstein temperature Θ_E, the second term the electronic specific heat, the third term anharmonic lattice specific heat and the last term magnetic specific heat.

In the case of Fe, it is still a relatively little known fact that at very low temperatures the FCC form of iron, i.e., the γ,

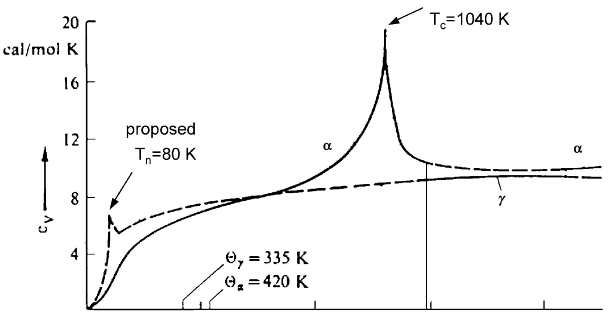

Fig. 3 Temperature dependence of specific heats of FCC and BCC forms of iron(17).

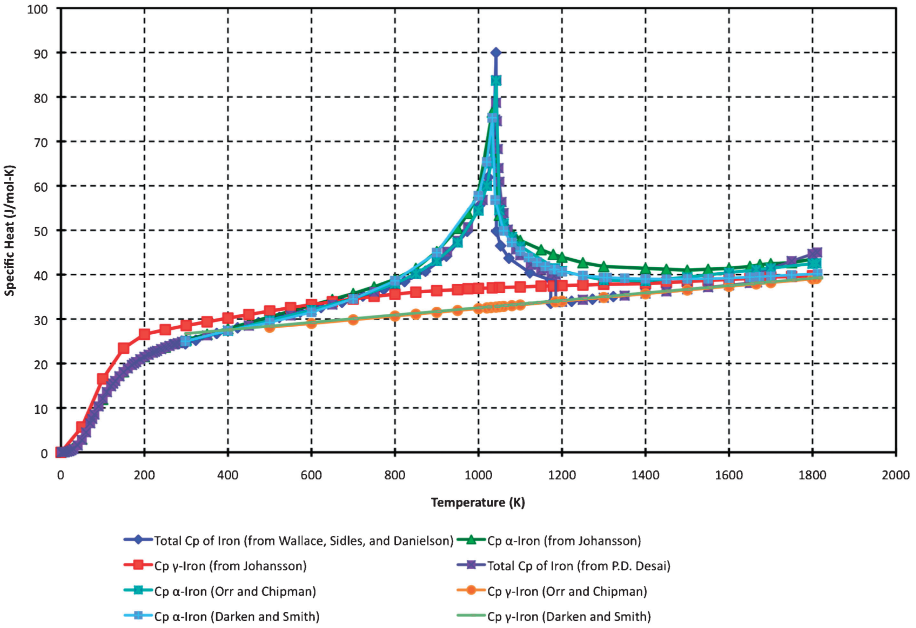

Fig. 4 Temperature dependence of experimentally measured specific heats of iron(18).

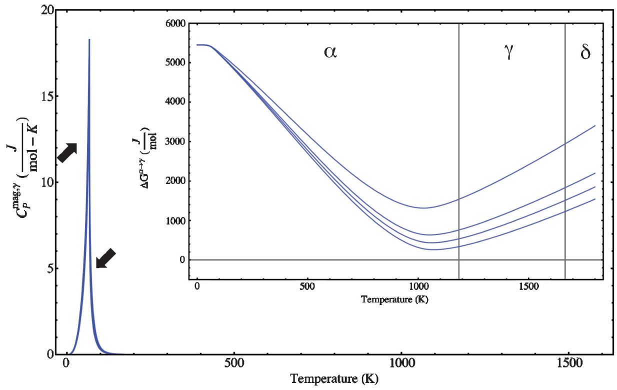

Fig. 5 Modeled height and shape changes of the Neel peak in the specific heats of gamma iron at low temperatures, and their effect on the related Gibbs free energies. The arrow on the left of the peak indicates height changes, and the one on the right indicates shape changes of the peak. The insert indicates the resulting changes in the Gibbs free energy difference $\Delta G^{\alpha\to\gamma}$ as a function of temperature between the α and γ forms of Fe(18).

metastable, but retained artificially(2)(17) is antiferromagnetic (AF). This is also confirmed by the observed $1/\chi$ trend with temperature in the γ phase which, when extrapolated to 0 K, cuts the temperature axis at a negative value. So, we may expect a Neel peak at low temperatures in the corresponding specific heat trend. Similarly, a Curie peak due to the ferromagnetic/paramagnetic transition at higher temperatures in the BCC (i.e. the α) form of Fe at 770℃ (1043 K) is a well documented feature in the measured specific heats. These trends are shown in **Fig. 3**, which is from Haasen's book(17).

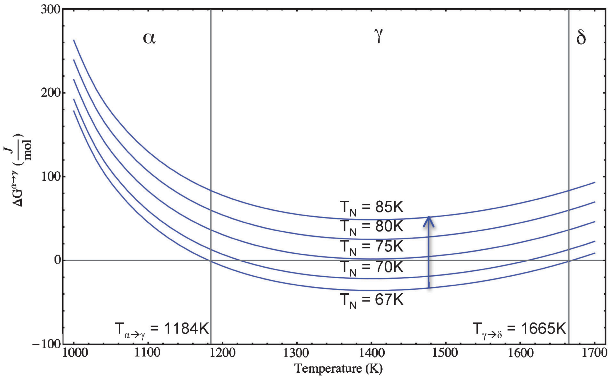

Fig. 6 Modeled changes in the Gibbs free energy difference $\Delta G^{\alpha\to\gamma}$ between the α and γ forms of Fe as a function of small temperature displacements of the Neel peak in the specific heat trend of FCC γ Fe(18).

The Neel temperature is indicated as a small peak, but it has not been studied in detail experimentally. A recent calculation(16) places the T_N at 67 K. The actual C_P data collected together for both phases is shown in **Fig. 4**(18).

Recently, we have modeled the competition for phase stability as a function of temperature between the α and γ forms of Fe by examining the effect of the magnetic peaks on the respective free energies of these phases and the resulting difference in the Gibbs free energy, $\Delta G^{\alpha\to\gamma}$. For the Neel peak in γ we introduced small changes in both the position and the shape of the peak, and for the Curie peak in α, where the temperature of the peak is well established, we introduced only small changes of shape compatible with the observed experimental data. **Figures 5 and 6** show the results of such modeling(18).

The situation may be considered as follows: Starting at 0 K, when the respective entropies of both phases may be assumed to be zero, the enthaply $H_\alpha < H_\gamma$ because the magnetic interaction in the ferromagnetic α is stronger than the interaction in the antiferromagnetic γ. As already mentioned, as temperature rises, the free energy of each phase is related to the specific heat (Fig. 3). A little above T_N, the paramagnetic γ phase will be even less stable compared to the (still ferromagnetic) α, but at higher temperatures the situation begins to change when the negative entropy terms ($-TS$), each related to the respective specific heat, increasingly come into play in the free energy of each phase. The modeling confirms that at the well documented phase transition temperature of 911℃ (1184 K), the $\Delta G^{\alpha\rightarrow\gamma}$ value becomes negative, as expected, but only by a very small amount. This indicates that it must be the Gibbs energy reduction in the gamma phase due the Neel peak at low temperatures, and the related$-TS$ term, that tips the balance. At still higher temperatures the BCC structure returns in the form of the delta phase at 1393℃ (1666 K), when the vibrational entropy effect in the 'more open' BCC structure imparts to it a comparable advantage. Thus, it can be argued that if the FCC γ were not AF at low temperatures, there would be insufficient free energy reduction for it to be stable at high temperatures when it is paramagnetic. Perhaps there is also an additional contribution to the specific heats of gamma iron from lattice harmonics, as argued some years ago by Zener(19). We should also be aware that T_N is likely to be a function of experimental details (dispersed particle sizes, stresses, matrix influences etc.), so until the magnitude of the Neel peak, its shape and form, as well as the exact temperature T_N, are well established experimentally, or the whole low temperature range modeled in still more detail, the above conclusion involves a certain degree of speculation. Our modeling indicates that raising the T_N by just a few degrees higher than 67 K eliminates the gamma phase altogether.

2. Phase Transformations

The area of Phase Transformations has been of great interest at different times in my research career. The field of phase transformations is also very large, like the field of phase diagrams, and many attempts have been made to classify transformations. Professor Jack Christian, my predecessor JIM gold medal winner, has made well known contributions here. Today, I would like to comment on two specific types of transformations. In the displacive (non–diffusional) phase transformations group, there is a subgroup sometimes referred to as ''*isothermal martensites*,'' and in the diffusional transformation group there is a subgroup known as the ''*massive transformations*'' (which I happen to have named more than 50 years ago(20)(21)). So, I will make a few observations on both of these small subgroups.

2.1 Isothermal Martensitic Transformations: –Is thermally activated martensite (TAM) a better term than isothermal martensite (IM)?

There is a very large literature on the *isothermal martensitic transformations*, including much work in Japan. Experimental work in this field typically involves kinetic studies, or structural studies, during cooling and reheating, with only a few experiments actually performed ''at constant temperature''. I will comment only on the terminology, the kinetics and the activation features of isothermal martensites. Recently, there was a symposium in the USA on phase transformations, just published this year(22).

The kinetics of martensitic phase transformations are usually designated as being either athermal or isothermal. *Athermal* implies that the transformation is not (hence the *A*) *thermally activated*, i.e., in an athermal transformation there is no thermal activation necessary for the transformation to proceed. Athermal transformations therefore do not depend on *time* but depend on the change in temperature. The word *isothermal* (*the same heat*) is used as an adjective for a transformation that occurs at a constant (same) temperature. When used in the context of martensitic transformations, isothermal refers to those transformations that proceed with time and are therefore contrasted with *athermal transformations* which require cooling or heating to proceed, and are not thermally activated(23)–(25). It is helpful to realize that the term *thermal* describes different concepts in the words *isothermal* and *athermal*. In isothermal, *thermal* implies ''temperature'', while in athermal, *thermal* is short for ''not thermally activated''(23).

Although the literature contrasts *isothermal* with *athermal*, not all non–athermal transformations are necessarily thermal. There may be thermally activated processes which occur on continuous cooling. These have sometimes been called *anisothermal*(26) but the term is rarely used. In martensite which forms athermally, thermal energy is insufficient to initiate the transformation. Whatever the mechanism of the initiation of the transformation is, it cannot proceed by thermally influenced fluctuations. The athermal transformation is initiated at specific sites only after a large enough chemical driving force is generated by cooling to a large enough degree below the equilibrium phase transformation temperature. This thermodynamic driving force must overcome the elastic (plastic) energy which is in opposition to the initiation of the transformation at specific sites and at below M_s. Thermal activation implies a statistical probability, meaning the same site will not always be repeatedly the first one to initiate the process. This is unlike in some of the *thermoelastic martensites* where the same site has been shown to repeatedly initiate the process(27).

Since the isothermal martensites involve time as a major parameter, the T–T–T (transformation–time–temperature) diagrams have been used to depict the progress of a given transformation. The well known C–curve shape for the isothermal thermal activated precipitation reactions can be plotted on a *TTT* diagram as shown in **Fig. 7**. The time to form the new phase initially decreases as the temperature is lowered below the equilibrium transformation temperature, due to the decrease in the barrier to nucleation, ΔG^*, as shown in Fig. 7. This decrease in the nucleation barrier occurs because the thermodynamic driving force increases as the material is cooled to lower temperatures. However the time to form the new phase begins to increase at lower temperatures due to the lack of thermal energy necessary for diffusion to take place. In terms of the thermally activated processes, nucleation controls the upper region of the C–curve while diffusion controls the lower region of the curve.

The C–curve behavior on *TTT* diagrams depicting the thermally activated martensitic transformations (see **Fig. 8**) cannot be explained in the same way as precipitation transformations because there is little or no activation barrier to growth in thermally activated martensitic transformations. Of course all thermally activated processes must cease at 0 K, but the *TTT* curves for the thermally activated martensitic transformations bend back well above 0 K. Thus, it appears that the barrier to nucleation must also have the shape of a C–curve if it controls the transformation kinetics. Since this barrier has within it the elastic energy of the transformation, such an increase in the barrier can arise because of an increase in the elastic stiffness of the matrix at lower temperatures. This has been discussed by Lobodyuk and Estrin(28).

Laughlin *et al.*(23) have considered some possibilities regarding the role of thermal activation and summarize them in the form of **Table 1**, where I have also included the thermoelastic martensites for comparison. We suggested that the isothermal martensites could be conveniently renamed as thermally activated martensites (or TAMs)(23). The TAMs have thermal activation only at the initiation stage, because the subsequent growth stage normally occurs rapidly, and in a martensitic mode, without requiring thermal activation. Of course there could be TAMs which have thermal activation in

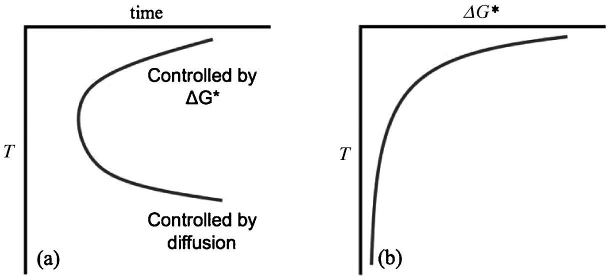

Fig. 7 Schematic of (a) a typical *TTT* curve for a diffusion controlled precipitation transformation and (b) a plot of ΔG^*, the barrier to nucleation, vs. T for precipitation(23).

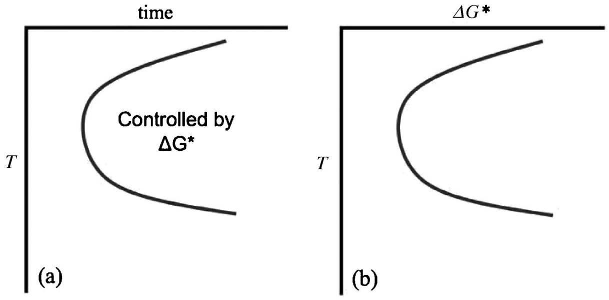

Fig. 8 Schematic of (a) a typical *TTT* curve for a thermally activated martensitic transformation and (b) a plot of the smallest ΔG^* for the given undercooling vs. T for a thermally activated martensitic transformation(23).

Table 1 Thermal activation of phase transformation processes.

		Thermal Activation for Initiation	Thermal Activation for Growth
I	Classical Precipitation	Yes	Yes
II	Thermally Activated Martensite (TAM) (on cooling, or at const. temp.)	Yes	No Yes?
III	Thermally Activated Martensite (Requiring Thermal Activation During Initiation and Growth)	Yes	Yes
IV	Athermal Martensite (AM) (substantially below T_0)	No	No
V	Thermoelastic Martensite (close to T_0)	No	No Yes?
VI	Diffusion Controlled Growth from Pre–existing Nuclei	No	Yes

their initiation process, as well as in their growth process. These also would show a C–curve behavior and would be difficult to distinguish from the normally observed ''isothermal martensites''.

In contrast, athermal martensitic transformations exhibit no activated processes and they do not need waiting time (incubation) to proceed, only a sufficient thermodynamic driving force obtained by lowering the temperature. A fifth possibility is also included in the table, namely one in which the initiation stage does not require thermal activation, but the growth stage does. This would also be the case for diffusion controlled precipitation reactions that grow from pre–existing nuclei. As pointed out by Laughlin *et al.*(23) and also by Lin *et al.*(29), it is of interest to note that there could occur sequences of martensitic transformations as shown in **Table 2**. These sequences can also be illustrated on the *TTT* diagrams.

As is well known, the majority of TAMs are studied during continuous cooling, or during cooling and subsequent holding at temperature. In Fig. 8 are shown progressions of different types of possible martensitic transformations. The relative position of the M_s and the nose of the TAM C–curve, and the rate of cooling allows for several possible sequences of transformations. In **Fig. 9**(a), the M_s temperature for athermal martensite has been placed above the knee of the *TTT* curve, but below the highest temperature at which TAM can form, M_{si}(23)(30). Cooling curve 1 represents the sequence of an athermal martensitic transformation followed by a TAM. In contrast to this, curves 2 and 3 represent transformations which proceed from athermal to anisothermal to isothermal. This is because the isothermal hold temperature was not reached before the material passed through the *TTT* curve, allowing for some thermally activated process to occur during the continuous cooling stage before the isothermal martensite begins to form(28).

Table 2 Possible martensitic transformation sequences.

Isothermal
Athermal → Isothermal
Anisothermal → Isothermal
Athermal → Anisothermal → Isothermal
Anisothermal → Athermal → Isothermal
''Mixed Athermal and Anisothermal'' → Isothermal

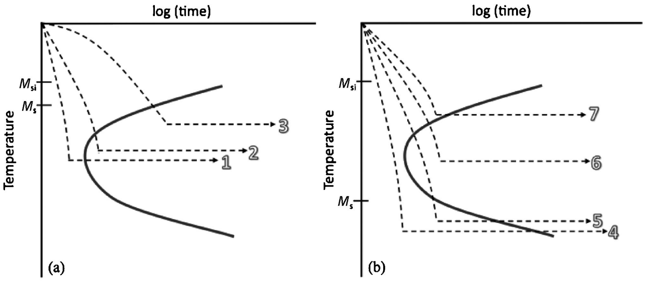

Fig. 9 Schematic of the possible sequence of different martensitic transformations with (a) M_s above and (b) below the nose of the *TTT* Curve(23).

Figure 9(b) shows a *TTT* curve in which the M_s temperature is below the knee of the *TTT* curve(23). Cooling curve 4 represents an overall transformation which starts as athermal one and after holding at a temperature below the M_s, and below the knee of the curve becomes isothermal in character. Curve 5 shows a transformation which starts as an anisothermal one, becomes athermal below M_s, but when held at a constant temperature below M_s and below the C curve knee, it becomes isothermal in character. Curve 6 represents a transformation which begins anisothermally and becomes isothermal on holding at a constant temperature above M_s. Finally, curve 7 represents an isothermal martenstitic transformation at a constant temperature. After holding at this temperature an athermal reaction could develop on further cooling below M_s, depending on how far the TAM has progressed.

So, since the isothermal martensite is a thermally activated martensite, perhaps the term isothermal martensite should be replaced with the more descriptive and more accurate term TAM. One can consider further possibilities if the C–curve for TAMs is displaced more to the left, eventually intersecting the temperature (*T*) axis. The transformation will then appear to be an athermal one since it occurs rapidly without any apparent incubation time. Such a transformation could be called a ''pseudo–athermal'' transformation. One way to distinguish this kind of transformation from a truly athermal transformation is to hold the sample at the temperature at which the transformation was first observed. If it does not proceed with time it is truly an athermal transformation. If, however, the transformation continues over an extended period of time it is seen to be thermally activated and hence it started as an anisothermal transformation. For more details see Refs. (22) and (23).

2.2 Massive Transformations: Can totally idiomorphic nucleation and growth occur in diffusional transformations?

Massive transformations have been studied since the late 1950's(20), and the actual definition of this type of transformation is still a matter of some discussion. However, in my brief comments today I would like to address mainly the crystallographic features and not the kinetics of this transformation process. One of the main questions regarding massive transformations has been whether or not there is a crystallographic orientation relationship between the parent phase and the product phase as the massive grains nucleate and grow. Such orientation relationships are almost always observed in diffusional transformations, and they are expected on the basis of activation energy arguments in the theory of transformations.

Based on the research information developed in the 1960's and 1970's, Christian included the massive transformation in his well known classification of transformations in metals and alloys in 1986(31). There, he concluded that massive transformations are "orientation free". In 2000, there was a Symposium on Massive Transformations (with 30 pages of discussion, interesting reading!(32) and I proposed there a definition for a massive transformation which seemed to cover all observed experimental features. In a later paper regarding the lack of orientation relationships between the parent (i.e. the matrix) and the growing massive phase in it, Laughlin, Soffa and I have concluded that there are indisputably clear cases where the growth of the product phase (i.e., the massive phase) is taking place as if it were occurring at a "free surface" of the growing grain, seemingly uninfluenced by the presence of the matrix phase ahead of it(33). We describe this type of growth as *idiomorphic*, and it implies a lack of crystallographic communication between the parent and product phases. This is illustrated in the schematic **Fig. 10**(33). A good example of an early X–ray demonstration of a complete lack of orientation relationships in Cu–Zn alloys is reproduced in **Fig. 11**(33). Subsequently, elegant electron microscopy studies have confirmed this feature in numerous investigations(32)(33). Some people have argued that this situation may be only occurring in alloys where there may be a change of chemistry (i.e. of bonding forces) taking place between the two phases at the interphase boundary, but idiomorphic growth has been so universally observed in typically metallic systems, like Cu–Ga, Cu–Zn or Ag–Al that this explanation seems unwarranted. However, at the atomic level, the studies now possible with the HRTEM techniques show that the idiomorphic massive (product) interface often involves very fine multiple crystal layers, referred to as facets, whose habit is that of the massive phase itself and not of the matrix as shown in **Fig. 12**(a) and (b). Many years ago, Prof. C. S. Smith(34) has suggested a parent/product interface possibility as shown in **Fig. 13**, and also in the schematic picture in Fig. 10. Recent HRTEM pictures confirm this possibility when the nucleation appears to take place at the parent phase boundary (**Fig. 14**(a) and (b)). However, during subsequent growth the idiomorphic feature is clearly seen in the HRTEM micrographs, confirming the existence of the type–3 (incoherent and irrational) interfaces(35). Faceting is frequently observed along such incoherent interfaces (for detailed references see Refs. (32) and (33)). In view of these recent symposia and discussions the most appropriate definition of a typical massive transformation seems to be best defined as follows: "*a composition–invariant, interface–controlled diffusional phase transformation, involving a characteristic patchy microstructure and frequent faceting and ledges, but not*

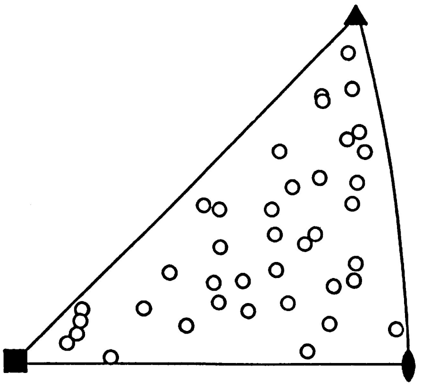

Fig. 11 Lack of orientation relationships (ORs) between matrix and massive grains in a partial massive transformation in a Cu–Zn alloy, as demonstrated by X–ray selective area diffraction(21).

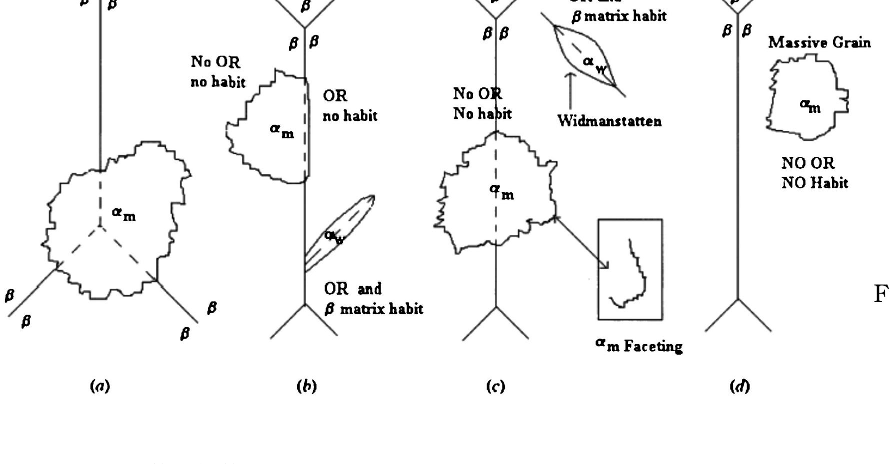

Fig. 10 Schematic types of various types of nucleation and growth that can occur in diffusional phase transformations(21).

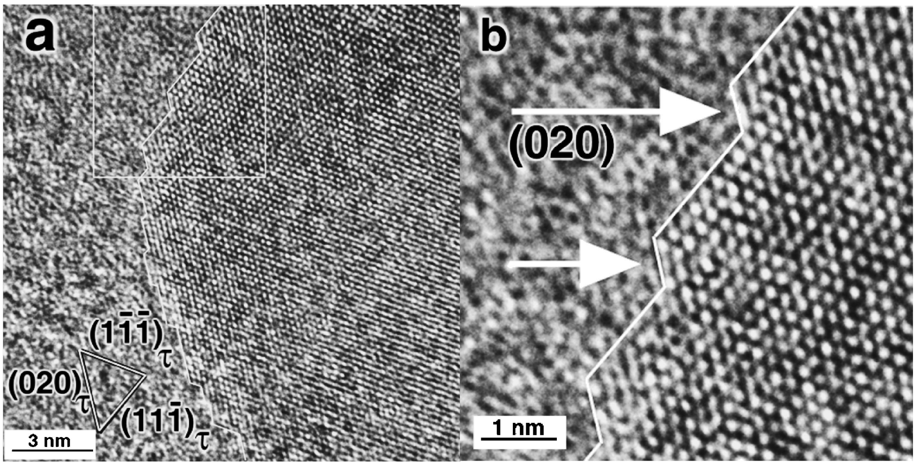

Fig. 12 (a) HREM image of a curved section of an ε–τ interface and (b) higher magnification of selected area showing composite (020) and {111} nanofacets/terraces/ledges$^{(33)}$.

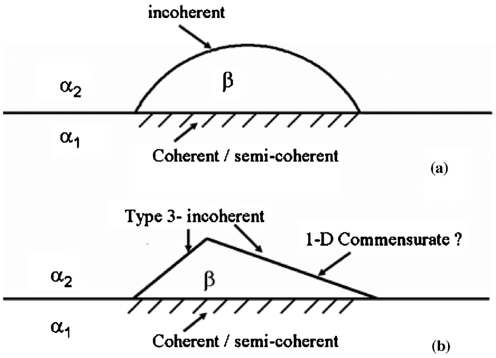

Fig. 13 (a) Classical critical nucleus model for singly faceted grain boundary nucleus which is incoherent with respect to grain α_2 but coherent or semi–coherent with respect to α_1. (b) Grain boundary nucleus involving faceting of the incoherent boundary segment$^{(33)}$.

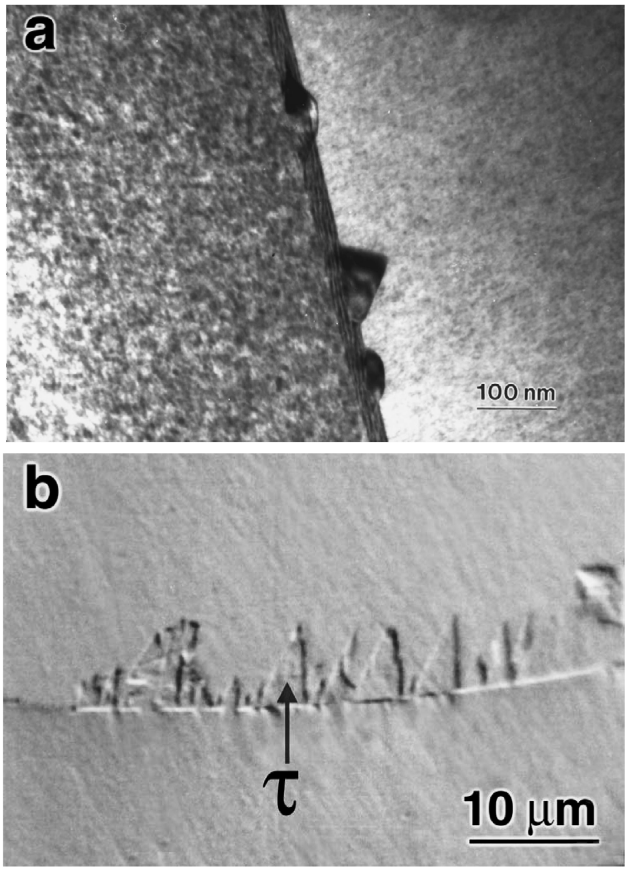

Fig. 14 (a) Grain boundary nucleation and growth of L1o τ–phase in Mn–Al–(C) alloy during massive transformation ε (hcp)→L1o. (b) Faceted grain boundary idiomorphs with Burgers OR with respect to one grain and apparent incoherent boundary with respect to the other. Growth is restricted along the semi–coherent boundary segment with the Burgers OR, but occurs readily into adjacent grain$^{(33)}$.

necessarily involving lattice orientation relationships."$^{(21)}$. A suitable name for the idiomorphic massive phase product has not been established.

So, these various forms of massive transformations continue being studied with increasingly sophisticated techniques and present a real challenge to researchers, also in Japan where the massive transformation has been studied very little. The overall conclusion at present is that *isomorphic massive transformations* are a specific unique feature and that there can be diffusional transformations that show no orientation relationships, i.e. no communication between parent and product phases, both in the nucleation and growth stages.

Acknowledgments

My friends in Japan know well that in my long research career I have been involved in many diverse topics in the wide field of Materials Science. In this presentation, I have touched on just a few subjects that may be currently of interest, and with which I have had a personal connection. This also enables me to mention a few scientific dilemmas and controversies. Since this is an invited lecture I have written it in 'first person' style.

I wish to express many thanks to my colleagues Professor Uichiro Mizutani in Japan and Professor David Laughlin in the USA for many stimulating discussions and for their help in the preparation of this manuscript.

I feel deeply honored and moved by the award of the Japan Institute of Metals gold medal. I also feel very proud to join your Institute as Honorary Fellow. Thank you very much for selecting me for both of these special honors. Your invitation to present an invited lecture in this connection is a special challenge. I have covered a lot of topics in this presentation and I hope that I have provided some of you with food for thought and for future research on some of the fundamentals aspects and on terminology in materials science. If this happens I shall be richly rewarded both by the JIM medal and your kind attention today.

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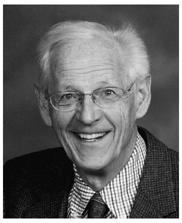

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