THE MECHANISMS OF SHAPE-MEMORY

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Abstract – Historically shape-memory phenomena have been thought to exist only in ordered alloy systems which exhibit thermoelastic transformation to twinned martensitic products. However, it is now known that this is not always the case, and that there are a number of different ways in which a material can fulfil the more general requirements for shape-memory. This paper reviews these requirements and illustrates how a range of transformation types can fulfil these criteria and therefore exhibit shape-memory behaviour.

1. Introduction

This symposium differs from the previous european meeting in that it concentrates entirely on the shape-memory phenomena associated with martensitic transformation. It is therefore appropriate that the mechanisms responsible for shape-memory be considered.

Before continuing further it is perhaps useful to describe the common 'shape-memory' effects. An example is illustrated in figure 1. This shows the so called 'one-way' effect where a material apparently plastically deformed at one temperature will return to its original form when the temperature is raised. The memory 'element' therefore "remembers" its shape prior to deformation. One-way memory was the first effect of this type to be identified, however, it was soon discovered that by suitable thermomechanical processing the same alloys could be "trained" to exhibit 'two-way memory'. These materials "remember" two configurations and will undergo spontaneous shape-changes between these two "memorised" states on heating and cooling. If one also employs a wider definition of 'shape-memory' it is possible to include other behaviour within the same general framework. Such properties include superelasticity, where large recoverable strains can be introduced into materials (ie effectively a "mechanical" shape-memory).

In the early days of shape-memory it was believed that there were strict structural prerequisites required of a memory material. These included that it should exhibit a martensitic transformation, that such transformations should be thermoelastic, and that the martensitic products should be crystallographically ordered and internally twinned /1/. These criteria were developed as a result of experimental investigations on early shape-memory alloy systems eg NiTi, CuZnAl, CuAlNi. However, it is now clear that shape-memory phenomena are not

restricted to systems exhibiting such limitations and that there are a
number of different ways in which a material can fulfil the requirements
for a shape-memory.

In a recent review Van Humbeeck /2/ considered 'shape-memory phenomena'
using an extremely general definition which encompassed both "classical"
behaviour (ie shape-changes on heating and/or cooling) and "shape-memory
at constant temperature" (ie superelastic effects). This review
summarised the reported mechanisms for these different facets of memory
behaviour and table 1 reproduces the principal mechanisms identified for
these effects. It is clear from table 1 that shape-memory can occur by
a wider range of mechanisms than previously thought, including via
transformation routes which are not martensitic. The presence of shape-
memory in such systems suggests that the prerequisites for memory
behaviour are more fundamental than the simple presence of a martensitic
transformation, and it is simply certain features of martensitic
transformations which fulfil these criteria. The aim of this paper is (i)
to identify these fundamental requirements, (ii) to illustrate how
martensitic transformations fulfil these criteria, and (iii) to show that
these general requirements can also be met by other types of solid-state
transitions.

2. Shape-Deformation.

The primary requirement for a shape-memory effect is some form of
temperature (or stress) -induced structural transition which exhibits a
transformation strain with a substantial deviatoric (or inhomogeneous)
component. During such a transition the strain associated with the
transformed volume can then be used to generate a macroscopically
observable strain. This fundamental property is illustrated in fig 2 for
the example of a martensitic transformation. According to
phenomenological theory /3,4/, the lattice deformation associated with
a martensitic transformation can be decomposed into two components, one
parallel to the invariant or habit plane, and a second normal to this
plane. The first is a shear strain which involves no volume change, and
the second is simply the volume change associated with the structural
transition. It is clear that such martensitic transformations have a
substantial deviatoric strain component (the shear) which is the
underlying reason for the transformation's ability to demonstrate a
shape-change.

However, martensitic transformations are not the only structural
transitions which are able to exhibit such effects. For example, under
circumstances where the thermodynamic driving force is insufficient to
allow martensitic transformation some compositional partitioning may
increase the driving force sufficiently to allow an alternative phase
change /5/. Because of the diffusional requirement, such transformations
cannot be classed as martensitic (which are diffusionless in character),
but can still be displacive and shear-like, with a coherent or
semicoherent interface. Such transitions are normally described as
bainitic. The relative importance of the displacive and diffusional
contributions in such transformations have been the source of significant
debate /6,7/. However, it is now clear that in a number of cases the
inherent shear-like nature of the bainitic transformation enables this
structural change to function as a viable mode of deformation /8/. In
principle it can therefore offer the potential of shape-memory
behaviour.

The transitions illustrated so far are martensitic or 'quasi-martensitic'
in nature. However, there are still further types of transformation which

also demonstrate similar deviatoric strain components. An example of such a transition is that observed in alloys based on the intermetallic compound Ni-Ti. These alloys exhibit a phase transition prior to the widely known martensitic transformation which involves two processes. The first is a transition from the parent phase (CsCl-type B2 superlattice) to an incommensurate phase. This is then followed by second stage transformation to a rhombohedral or R-phase. During the first transition the lattice does not change. However, it does on formation of the R-phase which can essentially be produced by an elongation of the B2-phase along any one of the $<111>_{B2}$ directions /9/. The R-phase transition therefore also produces the type of lattice change which can result in macroscopic deformation and the possibility of a shape-memory. This type of transformation is interesting since it is essentially second-order in nature /10/ and is therefore quite different from the martensitic transformations usually considered to be responsible for shape-memory behaviour.

As can be seen from table 1 martensitic, bainitic and R-phase transformations are responsible for most observed shape-memory phenomena. However, for completeness one further mechanism should be mentioned. This is twinning. The shape-deformation associated with twinning is particularly relevant to the 'mechanical memory' or rubber-like behaviour of martensites, and to the one-way memory effect in many shape-memory alloys. The lattice geometry across an interface between twin-related regions has many features similar to those discussed for martensitic transformations. For example the twinning modes of a system are selected on the bases (amongst others) of minimisation of the homogeneous twinning shear, and production of an undistorted interface structure /11/. Structural transitions associated with twinning can also therefore offer the shape-deformations essential for shape-memory effects.

It is clear that martensitic transformations are not unique in their ability to generate shape-deformations and that a number of other mechanisms offer similar possibilities. However, it must be stated that there are a number of other requirements which a system must fulfil before it can exhibit a fully-fledged shape-memory.

3. REVERSIBILITY OF THE STRUCTURAL TRANSITION.

An additional requirement which was originally considered to be a prerequisite for shape-memory was complete reversibility of the structural transition. It is easy to see how such an idea developed since, for example, in the two-way effect the shape-changes on heating and cooling must result from the forward and reverse structural transitions. Since such shape-changes are reversible, the structural transition responsible for the effect must therefore itself be reversible. The requirement of a substantial reversible shear component has led to the widespread idea that shape-memory must always be associated with systems exhibiting thermoelastic martensitic transformation. However, there is now substantial evidence that this is not always the case.

There is no doubt that the presence of thermoelastic martensitic transformation in an alloy system offers a means by which two important prerequisites (shear strain and reversibility) can be fulfilled, and that such transformations underpin the memory behaviour of a large number of alloy systems. Such systems include the familiar non-ferrous alloys eg Ni-Ti /12/, Cu-base ß-phase alloys /13,14/, and a number of the newer Fe-base shape-memory materials eg FePt, FePd,and FeNiCoTi /14,15,16/. An

additional feature of many of these thermoelastic martensitic alloys (particularly the non-ferrous alloys) is that they are also ordered, and this has clearly contributed to the much quoted requirement that shape-memory alloys be ordered. This latter requirement has now been shown to be incorrect, particularly in some of the ferrous alloys (eg FeNiCoTi) since these are crystallographically <u>disordered</u> and yet exhibit thermoelastic transformation. The question of thermoelasticity in these ferrous alloys is interesting since the elastic accommodation of the transformation strain cannot result from the inherent resistance of ordered structures to dislocation motion. Instead other mechanisms must contribute to the parent phase's resistance to plastic deformation. In these disordered alloys this can be achieved by heat-treatment which can increase the matrix flow stress by fine-scale coherent precipitation eg γ_2 in FeCoNiTi alloys /17/. In such systems this precipitation hardening of the parent phase results in an accumulation of elastic strain during transformation to thin-plate martensite. This produces high mobility martensite interfaces and thermoelastic transformation. In practice the much-quoted requirement of an ordered structure is therefore often simply a manifestation of the difference between thermoelastic and non-thermoelastic systems (eg in ordered FePt alloys martensitic transformation is thermoelastic, whereas in the disordered form the transformation is non-thermoelastic /18/).

However, thermoelastic martensitic transformation is not unique in its ability to produce reversible shape-changes. Examples which explode this myth are again the newer Fe-base alloys eg FeNiC and FeMnSi. These exhibit shape-memories based upon non-thermoelastic martensitic transformations /19,20/. These examples show that even thermoelastic transformation is not a prerequisite for shape-memory, and that a more fundamental requirement must be that of complete crystallographic reversibility during the transformation. Such reversibility can be observed in both thermoelastic and non-thermoelastic systems, although it must be stated that the thermal hysteresis for both the transformation and shape-strain will be larger in a non-thermoelastic alloy.

The examples described above have shown that reversibility of the structural transition is a key requirement for one and two-way shape-memory, and that a thermoelastic martensitic transformation with an ordered product need not be the only solution to these requirements. This can be further illustrated by considering structural transitions other than martensitic transformations. Such an example is that of the R-phase transition which is non-martensitic and reversible. Such a transformation therefore also offers an alternative mechanism by which the twin criteria of reversibility and shape deformation can be fulfilled. Similar remarks can also be made about twinning as a source of reversible shape strain. In 'conventional' twinning the shape deformation is usually considered to be a 'plastic deformation' process since the strain is non-recoverable. However, in principle there is no reason why the deformation should not be recoverable. This will simply depend on the mobility of the twin interfaces in a manner similar to that present during martensitic transformation. Twinning can therefore offer a means of generating recoverable shape deformation as long as the shape strain associated with the twinning process is accommodated elastically (analogous to thermoelastic martensitic transformation).

The premise of this section has been that 'memory phenomena' are based on reversible transitions. However, one can envisage an effect where the memory strain is only required in a one-off non-repeatable manner. In this case the structural transition on which the memory effect is based need not be reversible, and simply requires a transformation which generates a shape strain in a non-reversible manner. An example of such

a transition is the bainitic transformation. In principle if on heating, a metastable parent phase undergoes bainitic decomposition in a controlled manner (eg Cu-base ß-phase alloys /8/), the shape deformation associated with the bainitic transformation could produce a macroscopic strain and form the basis of a memory effect. Such a memory would operate in a 'one-shot' manner since the bainitic transformation is non-reversible due to the diffusional partitioning associated with the structural transition.

This section has attempted to review the often-quoted requirement that a shape-memory effect is only observed in thermoelastic ordered martensitic alloys which exhibit highly reversible transformations. It is clear that this need not be the case and that although in many common shape-memory alloys this type of transformation forms the basis of their memory behaviour, there are now a number of materials which exhibit similar shape-memories via either other types of martensitic transformation or other non-martensitic processes. However, a fundamental requirement of all these transitions must be that they are based on a reversible transition which exhibits a substantial shape-strain.

4. TRANSFORMATION PATHWAY..

The transformation characteristics discussed in the two previous sections exist in a wide number of systems. However, these do not always exhibit shape-memory. This is because there is one further important constraint that a system must fulfil before a shape-memory can exist. This is the ability to control the transformation pathway. This is one of the more fundamental pre-requisites for shape-memory since it is the means by which the transformation strain is converted to a macroscopic shape-change.

The simplest way to illustrate the importance of this feature is to consider the two-way memory in a thermoelastic martensitic alloy. If such an alloy is conventionally thermally transformed and then reverted to parent phase, there is no macroscopic shape-change. This occurs despite the fact that the forward and reverse martensitic transformations involve a transformation strain. The underlying reason for this effect is the transformation pathways adopted by these alloys which occur via a number of crystallographically equivalent routes. This produces a number of microstructurally distinct martensite variants which each exhibit different orientations of the transformation shears with respect to that of the parent phase /21/. The result is a mutual self-accommodation of the transformation strains which gives rise to no net macroscopic shape-change. Such effects are present in a number of the transformations discussed in section 2, including thermoelastic martensitic, R-phase, and bainitic transformations. How then can a macroscopic shape-change be developed in such systems? The solution is to influence the transformation pathway so that the structural transition takes place via a limited number of routes, thus restricting the number of crystallographic variants formed. This will then minimise the extent of self-accommodation, and therefore maximise the macroscopically observed strain /22/. This limitation of transformation pathway can be brought about by a number of mechanisms. However, these all have a common feature. This is the influence of stress on the microstructure of the transformed volume.

The effect of stress on structural transitions is illustrated in figures 3a&b using a general Landau approach /23/. These figures show schematically the dependence of a one-dimensional free-energy function on the characterising order parameter and temperature. In the context of

the present discussion the order parameter represents strain (ie transformation strain) and although the function should strictly apply only to second-order transformations, the qualitative features of this approach should apply to first order transitions as well. Figure 3a shows that under stress-free conditions, below a critical temperature, T_c, two free-energy minima exist which represent two thermodynamic 'solutions' to the transformation. These two stable states are analogous to the multiple variant situation present during stress-free transformation in a number of the systems discussed above, and leads to self-accommodation of the transformation strain. Figure 3b is interesting however, since this adds the presence of stress as an external variable. Under such circumstances the 'solution' is no longer two equivalent variants, but instead one variant is stabilised with respect to the other. In other words considering a more general case, stress selects a limited number of variants and thus essentially limits the transformation pathway. The Landau approach describes this effect phenomenologically, however, such observations have also been made experimentally. For example external stress will stabilise martensite variants on the basis of the orientation of their transformation strains with respect to that of the imposed stress /24/. A key point is therefore how can the effect of stress be used to explain the presence of memory behaviour?

It is clear that the presence of stress during a transformation will break the symmetry of the transition and produce a transformed volume containing only structural variants which are stabilised by the stress field. The presence of a transformed volume containing a 'predominant variant' morphology (ie non-self accommodating) <u>must</u> therefore result in a macroscopic shape-change. Such an effect forms the basis of the shape change during forward transformation in two-way memory and during superelasticity by transformation. Such effects can thus be produced via any of the transitions described in the previous sections provided that stress is present. The origin of this stress is clear during superelastic deformation. However, what is the nature of the stress-field during two-way memory (where the effect takes place without the presence of externally applied load) ? In this case the stress field is present in the form of internal stress which results from microstructural features within the parent phase. Numerous examples of such 'stress-centres' have been observed to control subsequent transformation. These include dislocation debris /25,26/, various types of precipitate /27/, and transformation products stabilised by previous transformation cycles /28/. In all three cases these features are introduced by some form of thermomechanical processing which is known generically as "training".

During both superelastic deformation and two-way memory reversal of the driving force (ie unloading or heating) results in an inverse shape-change. How is such a reverse shape-change produced? In both phenomena the reverse transformations do not proceed by renucleation of the parent phase, but instead by reversion of the transformation products. Under such circumstances the reverse shape change therefore arises since the predominant variant morphology reverts to parent phase via the inverse of the original transformation pathway. The key to this behaviour is again the limitation of the transformation pathway. The exact mechanism of this reversion depends on the type of transformation employed for the effect. For example in martensitic alloys it arises from shrinking of the highly mobile martensite interfaces, and in R-phase transformations from the decreasing tetragonality of the transformed volume. In most systems however, this limitation of reversion pathway arises from a combination of transformation symmetry effects, and minimisation of the free-energy of dislocation "debris" produced during the forward transformation.

Two further types of memory phenomena must also be considered in addition
to those described above. These are pseudoelastic deformation and shape-
memory on heating (ie one-way memory). The source of these phenomena are
more subtle than those described in the previous two examples and result
from the effect of <u>externally</u> applied stress on the products resulting
from a self-accommodating transformation. It is clear from figure 3a that
under stress-free conditions the self-accommodating morphology is the
thermodynamically stable variant microstructure below a critical
temperature. However, if stress is applied to such a morphology below T_c
certain variants will become destabilised with respect to others (fig
3b). If the variant interfaces are mobile, the transformed volume will
then be converted from a self-accommodating morphology to one containing
a predominant variant. This will result in a shape change. Such
transitions can therefore act as a deformation mechanism. The details of
such transitions vary from system to system and can result from
interconversion of twin-related regions <u>within</u> variants (eg AuCd and
InTl) or from interconversion of twin-related variants (eg Cu-base
martensites and R-phase variants). In both cases the deformation
essentially results from the shape-change associated with twinning. If
such transitions are fully reversible on unloading, ie the twin
interfaces are mobile, this forms the basis of pseudoelastic deformation.
However, if this deformation is essentially non-recoverable it then
provides the basis for a one-way memory.

The key to the one-way memory effect is the reversion pathway adopted by
these stress-reoriented microstructures on heating. In practice, the
predominant variant structure produced by reorientation simply reverts
to parent phase by a transformation pathway which is the inverse of the
original thermal transformation. This limitation of the reversion pathway
arises due to the same structural effects discussed for two-way memory
and superelasticity, and returns the original parent phase orientation.
It also produces a shape-change which is the inverse of that introduced
by variant reorientation during the deformation stage.

5. SUMMARY.

Historically shape-memory phenomena have been thought to exist only in
ordered alloy systems which exhibit thermoelastic transformation to
twinned martensitic products. It is now clear that these prerequisites
are only one way in which the structural requirements for shape-memory
can be fulfilled. In practice the requirements are more fundamental than
those described above, and in their most general form are that the alloy
system (i) must exhibit a structural transition which exhibits a
significant inhomogeneous strain component, (ii) the transformation must
generally be reversible (although this need not necessarily be the case
in all memory effects), and (iii) there must be the possibility of
limiting the transformation pathway so that the inherent shape-strain of
the transformation can be converted to a macroscopic deformation.

It is clear that in practice all three criteria can be met by martensitic
alloy systems particularly where the transformations are thermoelastic.
However, alternative structural transitions can also fulfil these
criteria. These include R-phase, twinning, and bainitic transformations.
In all these transformations the key to memory phenomena is the
possibility of limiting the transformation pathway. In each system this
is brought about by a slightly different mechanism, but in general it
results from the effect of external or internal stress on <u>either</u> the
pathway adopted during transformation, or on the variant morphology of
a transformed material. With these general requirements it is clear that
there now exists the possibility of shape-memory in a wider range of
materials. Such materials could include ceramic and biological systems

as well as more conventional metallic alloys.

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TABLE 1

| Shape-Memory on Heating	1. Martensitic Transformation (m→p) 2. Decreasing Tetragonality (c/a) e.g. R-phase 3. Bainitic Transformation

Shape Memory on Cooling	1. Martensitic Transformation
	     a. growth of stabilised variants
	     b. nucleation and preferential growth
	       at "oriented" defects.
	 2. Rhombohedral Transformation

Shape-Memory at Constant Temperature	1. Martensitic Transformation e.g.
	     Superelasticity by transformation.
	 2. Twinning-Related Variant to Variant
	     Conversion e.g.pseudoelasticity/
	     rubber-effect
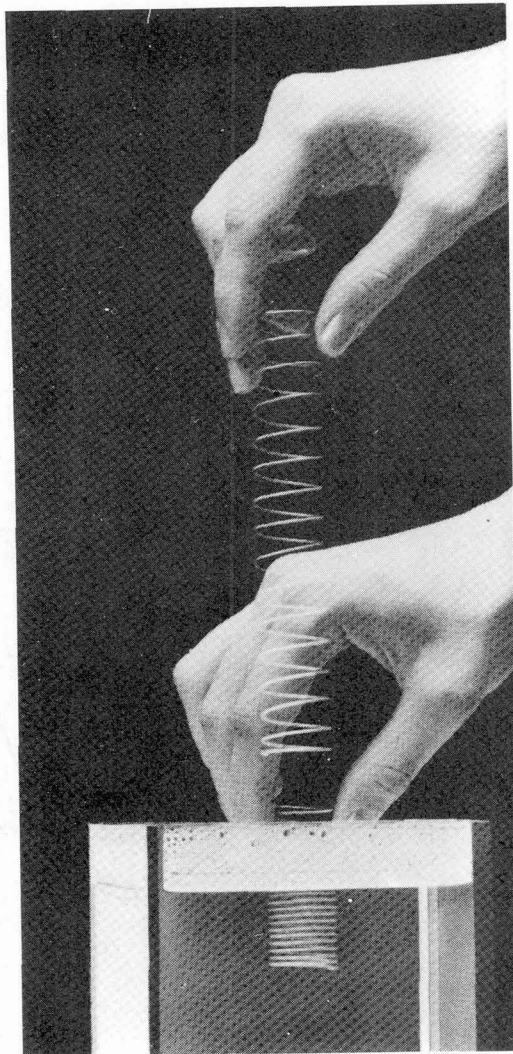
Figure 1 - A Ni-Ti <u>one way memory</u> spring deformed to several times its original length will spontaneously return to its original shape in hot water. (Tokin Corporation)
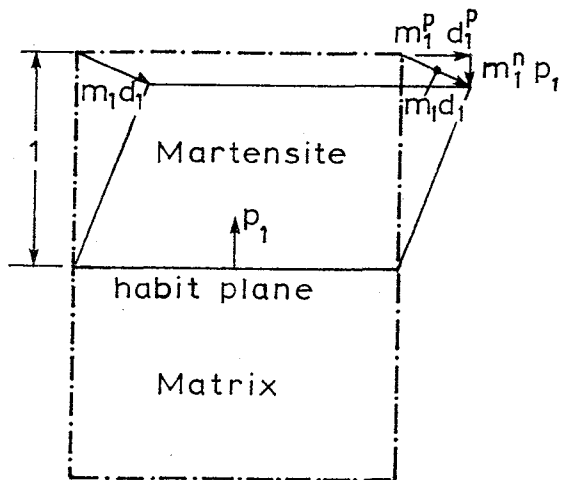
Figure 2 - Illustration of the resolution of invariant plane strain into two components.
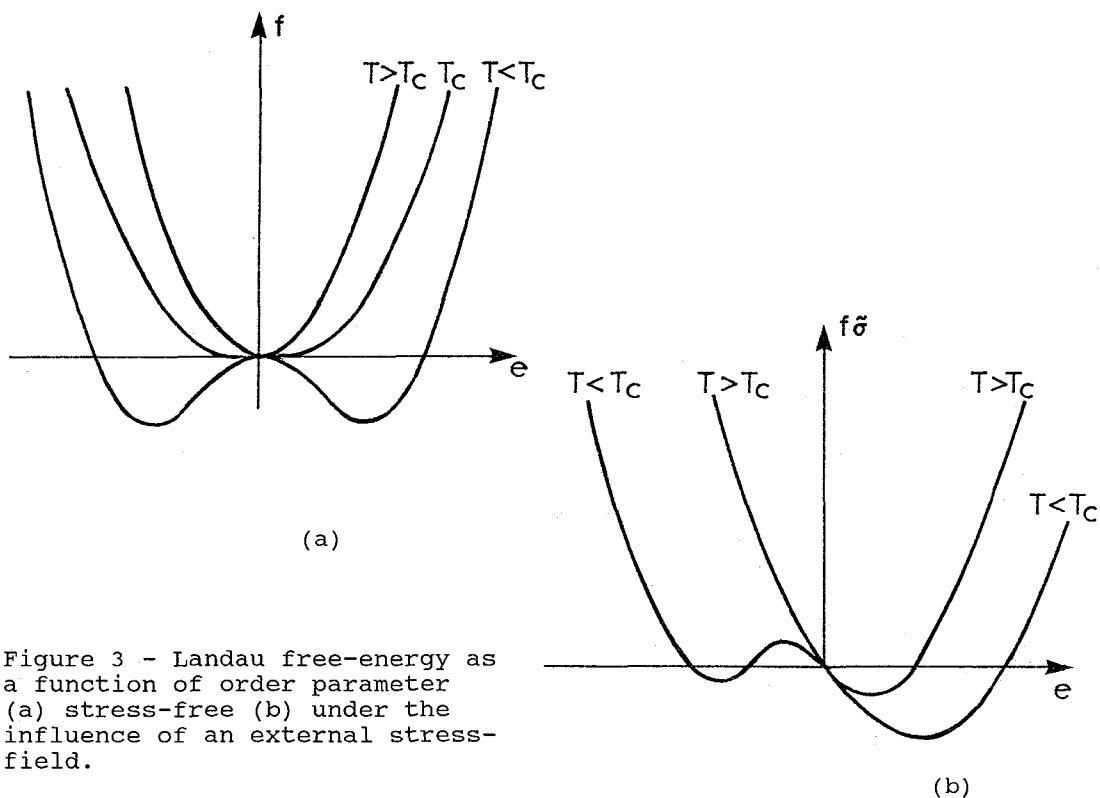

(a)

(b)

Figure 3 - Landau free-energy as a function of order parameter (a) stress-free (b) under the influence of an external stress-field.