



REVISTA SAM

Publicacion de la Sociedad Argentina de Materiales

A black and white micrograph showing a complex, layered, and somewhat chaotic structure, characteristic of a martensitic transformation in a material. The structure consists of numerous parallel, slightly curved bands or lamellae that are oriented in different directions, creating a textured appearance. The bands are separated by darker regions, and the overall pattern is dense and intricate.

The martensitic transformation

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Diciembre 2004 - Volumen 1 - N° 3

www.materiales-sam.org.ar

Registro N°ISSN 1668-4788



Editorial

En junio del corriente año encarábamos la reedición de la REVISTA SAM (anteriormente denominada «Metalurgia Moderna»), como Revista Oficial de la Asociación Argentina de Materiales, de carácter virtual, dedicada a la difusión del conocimiento relacionado con la Ciencia y Tecnología de los Materiales.

Hoy publicamos el Número 3 de 2004.

La revista ya fue leída por 2566 personas !!!!!!!

Realmente estamos muy contentos y orgullosos de este logro.

Por este motivo queremos agradecer a todos aquéllos que contribuyeron a la REVISTA SAM.

En primer lugar a los autores de los trabajos: Robert Cahn, Luis de Vedia, Noemí E. Walsóe de Reca, Miguel Ipohorski y Manfred Ahlers, por el alto nivel y claridad de sus artículos. Al INTEMA-Universidad Nacional de Mar del Plata, a la Facultad Regional de Concepción del Uruguay – Universidad Tecnológica Nacional y a la Facultad de Ciencias Exactas, Químicas y Naturales-Universidad Nacional de Misiones, por sus contribuciones que permitieron lograr un mejor conocimiento de dichos centros nacionales dedicados a la Ciencia, Tecnología y Formación de Recursos Humanos en el área de los Materiales. A los miembros del Comité Científico: Dr. Esteban Aglietti, Dr. Manfred Ahlers, Dr. Numa Capiatti, Dr. Eduardo Dvorkin, Dr. José R. Galvele y Dr. Roberto J. Williams por su valiosa colaboración. A Ramón Castillo Guerra, Liliana Roberti y Victor Fierro, por el excelente trabajo en la edición de la revista.

Agradecemos, también, a todos los Amigos de la SAM por apoyarnos y alentarnos en esta tarea.

Comisión Directiva

The martensitic transformation

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Resumen.

Se discuten algunos aspectos en la investigación y en el desarrollo de materiales que presentan una transformación martensítica. Se subdivide la discusión en base a cinco preguntas:

1. cómo puede nuclearse y crecer la martensita dentro de una matriz, siendo que los átomos no pueden reacomodarse por difusión, y a pesar de que, al ser la transformación de primer orden, hay coexistencia de fases con grandes cambios de estructura cristalina?
2. por qué ocurre la transformación a las temperaturas y composiciones observadas? Cuáles factores controlan la energía libre de Gibbs de las estructuras involucradas?
3. qué pasa cuando se permite difusión en la martensita? Cómo se relaciona la martensita con las fases de equilibrio?.
4. cómo se modifican las propiedades por tratamientos termomecánicos?
5. para qué aplicaciones serán útiles las transformaciones martensíticas?

Se dan algunos ejemplos de actualidad con referencia a estas preguntas, comprendiendo aleaciones con memoria de forma, como las aleaciones de metales nobles, aleaciones de Ni-Ti, aleaciones de Heusler ferromagnéticas y aceros. Se muestra que todavía quedan muchas preguntas por contestar.

Key words: Martensitic transformation, shape memory alloys

Introduction

When a gas, for example nitrogen is cooled, it transforms into a liquid at a temperature T_B , called the condensation or boiling temperature. The temperature T_B depends on the applied pressure p according to the Clausius –Clapeyron equation:

$$\frac{dp}{dT_B} = \frac{S_G - S_L}{V_G - V_L} \equiv \frac{\Delta S}{\Delta V} \quad (\text{eq.1})$$

S_G and S_L are the entropies of the gas and the liquid, respectively, and V_G and V_L are the corresponding volumes, all quantities taken per one mole. Although they seem not be so spectacular, phase transformations occur frequently also in the solid state, depending on temperature, pressure and other corresponding variables, similar to equation 1. In fact, they are often responsible for the properties that are sought after for technological applications. Several types of transformations are known. They can be classified according to the following scheme [1]:

- Transformations that lead to a redistribution of atoms, called civilian transformations by J. Christian, because they involve the individual atom movements by diffusion. These transformations are restricted to higher temperatures at which atom diffusion can take place.
- At lower temperatures, when the atom jumps are frozen-in, transformations nevertheless can occur, however not by the individual jumps, but by a cooperative movement in which the atom arrangements can change their volume and shape, but in which neighbors remain neighbors. J.Christian called them military transformations. Depending on the type and degree of distortion these diffusionless transformations can be further subdivided.
- In the dilatation dominant transformations only the volume changes. An example is the transformation between two face centered cubic structures in cerium.
- To another group of transformations belong those in which the lattice is distorted without involving a volume change. They are called deviatoric dominant and produce a strain when they are formed within the matrix.
- When the strain energy is large, the kinetics and morphology of the transformation is dominated by the strain energy, and the transformation is called martensitic.
- It has to be clearly distinguished from those in which the strain energy is small and does not dominate the transformation. These are denominated ‘quasimartensitic’ transformations.

Thus the martensitic transformation is a first order phase transition which is diffusionless and is associated with a large shape change. It is called first order, since the abrupt change from one structure, the matrix phase, to the martensite is associated with a change in entropy. Being a diffusionless transformation without a redistribution of atoms on the lattice sites, the configurational entropy remains invariant and only changes in vibrational entropy, and eventually changes from other degrees of freedom related to the conduction electrons are important. This is an important aspect that simplifies the evaluation of the martensitic transformation, compared to the diffusional transformations in which large changes in configurational entropy are often very difficult to evaluate with the required precision.

The study of the martensitic transformation in metals and alloys is a very active field of research. This is due, on the one hand, because it presents very interesting aspects in the understanding of the properties of the solid state. On the other hand these alloys have found wide applications in technology and medicine. In this short review some current problems of general interest are briefly discussed. Emphasis will be placed on the contributions that have resulted from the investigation of the Metal Physics Group in the Centro Atomico in Bariloche, Argentina. The paper is subdivided into chapters, each of which is introduced by a question.

1. How is it possible that the martensitic structure can nucleate and grow within a solid matrix phase without the possibility for the atoms to readjust themselves by diffusion, in spite of being a first order transformation with large changes in the crystal structure?

That this is an important problem can best be seen from the two-dimensional sketch of figure 1. The original high temperature phase is represented by the quadratic periodic array of circles representing the atoms (a). On cooling it transforms to a distorted new lattice, which can be described by the homogeneous

distortion, called the Bain distortion. Starting from the square lattice two equivalent new orientations can be obtained (b,c) which differ only in the orientation of the Bain distortion. This new structure has to nucleate within the matrix phase, without creating too much unfavorable distortion. How is this possible? This can best be illustrated by the observation of the transformation. In figure 2 is shown a sequence of photos obtained by transmission electron microscopy during cooling of a Cu-Zn sample in the microscope [2]. At the upper left appears a thin martensite plate that extends through the field of observation, upper right, together with the growth of two other plates. Subsequently the plates start to thicken by the lateral movement of the planar interface in the lower part of the figure. By diffraction analysis it has been shown that the structure within the plates is the fully developed martensite structure. Thus the transformation from one structure to the other occurs initially by the atom redistribution at the tip of the plates, followed by the rearrangements of the atoms at the expanding interface. Three types of questions arise immediately. First, what characterizes the planar interface, called the habit plane, that separates the thin martensite plate from the matrix. Second, what types of atom movements are permitted at the tip if any atom redistribution by diffusional processes is prohibited, and third under what conditions the habit plane can be displaced easily. It is evident that the habit plane must have a low energy, otherwise its unfavorable contribution could not be overcompensated by the decrease in volume energy of the more favorable martensitic phase.

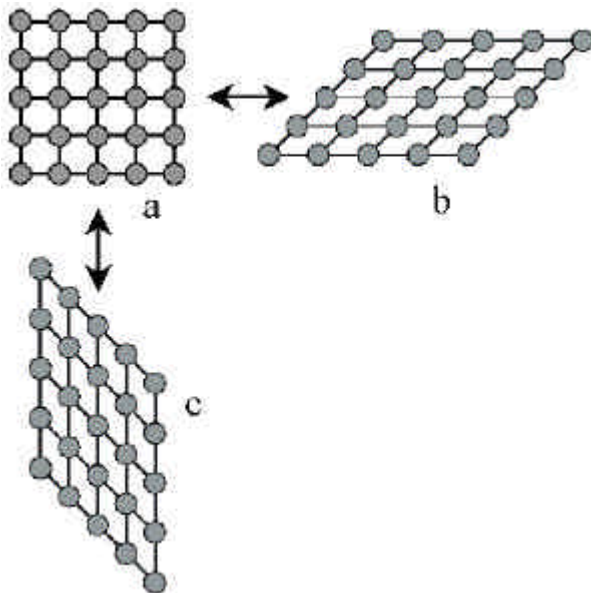


Figure 1. Two-dimensional sketch of a martensitic transformation from a square lattice (a) to two variants (b) and (c) that differ only in orientation.

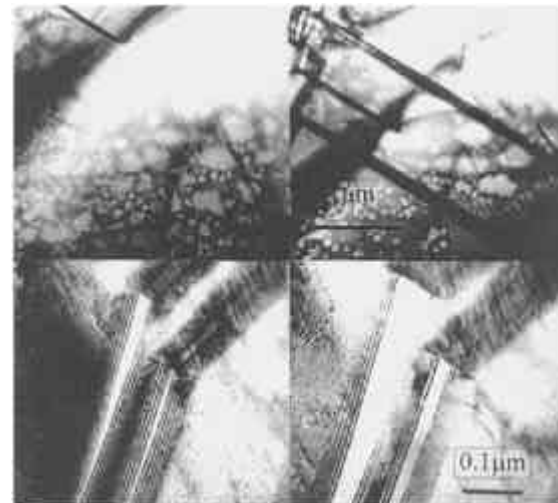


Figure 2. Observation by transmission electron microscopy of the growth of thin martensite plates (upper part) and their ensuing thickening (lower part) in a Cu-Zn single crystal during cooling.

A great progress meant the publication of the phenomenological theory by Wechsler, Lieberman and Read, and equivalently by Bowles and Mackenzie [3]. They postulated that on the average the habit plane must be free of elastic distortions. It implies that a part that is cut from the matrix phase parallel to the future habit plane and permitted to transform to the martensite must fit well after joining with the other part that remained in the matrix phase. This means that any vector lying in the cut plane must be unchanged in length and orientation. The change in structure can be described by a homogeneous Bain distortion of the original lattice, similar to that sketched in figure 1. It can be expressed by the length changes, i.e. the strains in three orthogonal directions. This distortion is not sufficient to obtain an undistorted habit plane. The authors therefore postulated that in addition the martensite must be deformed by a shear on an appropriate reasonable shear system. In this way it became possible to account for an undistorted habit plane between

the two structures and also for the other crystallographic quantities that can be measured. This phenomenological theory describes well the relationship between the structures, but does not pretend to give information on the atom movements during the transformation. Furthermore it needs a plastic deformation of the martensite, which requires an internal deformation stress.

The first attempts to describe the atomic movements during the martensitic transformations were made by Burgers in 1934 [4], but since he was not able to rationalize the observed transformation crystallography, his approach was not further developed. A full transformation theory has to take into account both aspects, the crystallography and the corresponding atom movements. How this can be done will be outlined in what follows.

To start with, a simple martensitic transformation shall be considered, whose mechanism is quite well understood. This is the change from the face-centered cubic (fcc) to the hexagonal (hex) structure by the movement of partial dislocations on the close packed lattice planes. Examples are Co and Ni-Co alloys. The fcc structure can be described by the stacking of close packed planes with the sequence ABCABC, with the B-layer atoms lying in the holes of those of the A-layer, and the C-layer ones on top of the A and B-layer holes. The transformation to the hexagonal structure with the ABAB sequence involves a rigid displacement of one layer with respect to the neighboring ones, which is achieved by the movement of partial dislocations on each second plane. The habit plane in this case is the basal plane and the whole lattice distortion during the transformation manifests itself in the shear parallel to the habit plane. Shape changes by the movement of dislocations on glide planes occur down to the lowest temperatures in the absence of diffusion, as is well known from the plastic behavior of metals. Therefore these types of martensitic transformations are nothing special, they can nucleate by the dissociation of parallel dislocations on each second close packed plane when the stacking fault energy becomes negative. They then move singly or as a group through the lattice with a certain friction. They create a distortion around them, which can be taken up by the surrounding matrix. Thus the question asked above can be answered very simply.

The answer is not so simple when other types of martensitic transformations are considered, for example the transformation from the bcc to the close packed fcc or hex martensite, or vice versa from fcc to bcc in the steels. Martensitic transformations are observed in a large number of noble metal alloys based on Cu, Ag or Au with the high temperature bcc structure, called the β phase. These alloys show generally a small hysteresis between the transformation on cooling and the retransformation during heating, whereas in the steels the hysteresis is very large, an observation that has also to be explained. The transformation in Cu-Zn shown in figure 2 can serve as the first example whose more detailed analysis will permit to answer the first question. This will be done now.

At high temperatures and at compositions around Cu-50%Zn the atoms are distributed at random on the sites of a bcc Bravais lattice, called the A2 phase. On cooling such an alloy, a long-range ordering to a B2 phase starts at a temperature T_{B2} . A B2 ordered β phase unit cell is shown in figure 3a. The occupation probability of the atoms at the corners becomes different from that in the center. This is the structure that starts to transform to the martensite on cooling at a temperature M_s that depends on composition. The transformation continues with decreasing temperature and is completed at M_f . As shown in figure 2 (above) the transformation starts with the formation of thin plates, and continues with their thickening (below). The growth of the thin plates looks very similar to that which is frequently observed for the fcc to hex transformation in the Co-alloys. However, the thickening of the plates is not found in the Co-alloys. The important fact is that the transformation is completed at the tip, as in the Co-alloys. Although the transformations look very similar in both cases, it is not possible to describe the transformation in such a simple way by the movement

of dislocations with partial Burgers vectors on low indexed glide planes, although formally a Burgers circuit around a tip can be made.

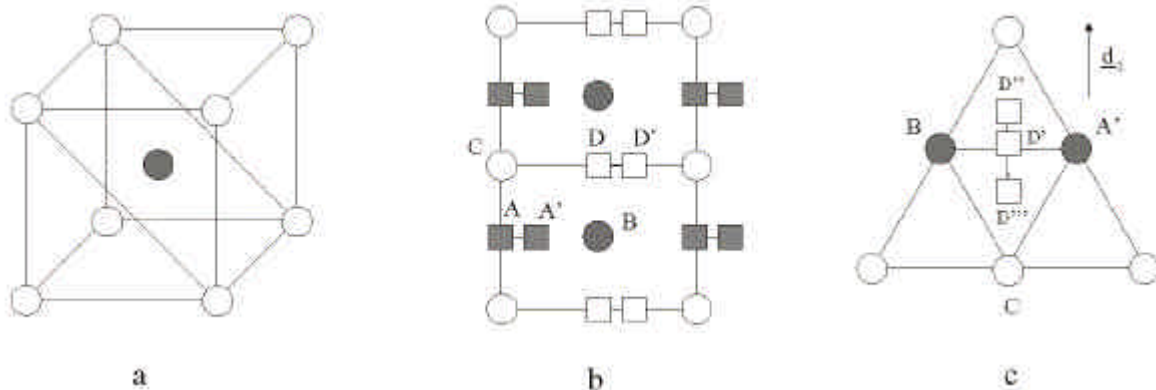


Figure 3. The transformation from a B2 ordered bcc to a close packed martensite. The original B2 lattice (unit cell in a) is sheared on the inclined (110) plane leading to the displacement of atoms as shown in (b). The square symbols denote the atoms on the plane above those of the round symbols, full and empty symbols characterize the Cu and Zn rich sublattice sites. During the shear A and D move to A' and D'. The shuffle consists of a displacement on an inclined plane (c) restoring the correct stacking by moving D' to D'' or double the distance to D'''.

How to treat this type of transformation has already been shown by Burgers [4]: A combination of two shears is necessary simultaneously at the tip. The only additional question that has to be asked is what are the most favorable shear systems. This aspect has been discussed [5] for a large group of transformations, permitting not only to rationalize the crystallography consistent with the phenomenological theory, but in addition to understand why a certain crystallography is favored. It seems to be reasonable to expect that those shears are the easiest that require the smallest distortion and friction energy. As in the Co-alloys and in general the shears for plastic deformation proceed by the movement of dislocations. They create a distortion field around them which is dependent on the elastic constants, and prefer to move on shear planes that offer the least resistance. When their movement is associated with a change in structure then the resulting shear system in the new phase should also be a favored system, which leads to the reasonable supposition that the whole transformation path requires little energy. For example, in the transformation from fcc to hex in Co, the basal plane is the preferred slip plane in the two structures.

In a hard sphere model the A2 and B2 structures are not stable. This can best be seen from figure 3b. There the diagonal plane of figure 3a is replotted and is marked by the round symbols. Atoms on the plane above (squares) come to lie in the middle above two atoms on the lower plane. This is an unstable configuration for hard spheres, which move to the neighboring position in the middle of three atoms below, as A to A' in the figure, or in the opposite direction. In reality the A2 and B2 structures are stable at elevated temperatures in many noble metal alloys based on Cu, Ag or Au. The reason is that the atoms can vibrate with higher amplitudes than in the displaced positions. This leads to a higher uncertainty in position, which means a higher vibrational entropy $\Delta S_v > 0$. Although energetically the unstable position is unfavorable, $\Delta H > 0$, the entropy term makes it stable, since it enters with an opposite sign into the Gibbs free energy $\Delta G = \Delta H - T\Delta S$, with T the absolute temperature. Only as long as the sign of the Gibbs free energy is negative does the B2 structure remain stable.

It is clear that with decreasing temperature B2 decreases in stability, and the tendency to a displacement (A to A' in the figure) increases. It manifests itself also in a decrease in the elastic shear constant $C' = (C_{11}$

$-C_{12}/2$ that describes small, elastic displacements between neighboring $\{110\}$ planes in the $\langle\bar{1}10\rangle$ direction (A to A'). Finally a collapse takes place, although C' can remain positive, and a transformation by a shear on each consecutive (110) plane with Burgers vector $(a/8)[110]$ becomes favorable. This shear alone does not produce the martensite lattice, at variance with the analogous case for the fcc to hex transformation. That a structure with only this type of shear can be stable though has been observed in the form of small precipitates during the dezincification of Cu-Zn at elevated temperatures [6]. But it is very easy to get to the observed martensite structure by adding small displacements on an inclined plane. During this first shear in the same direction on each consecutive plane, which will be called the "primary shear", an inclined (011) plane is transformed into a close packed plane that has already the structure of the martensite phase. The atom distribution on this inclined plane is shown in figure 3c. However the stacking is not correct. The plane containing atom D' above that of the round symbols has to move, indicated by D' to D'' or twice the distance to D''', to get to the correct stacking corresponding to a close packed structure. These are only small displacements, called "shuffles" of one plane with respect to the neighboring one.

The atom movements are illustrated by a hard sphere model in figure 4. Three consecutive (110) planes are drawn, the filled and open circles indicate the B2 order. In (a) the original B2 lattice is shown, the dashed triangle characterizes the inclined (011) plane. The primary shear leads to the configuration in figure 4b. As can be noticed, the dashed plane has become a close packed plane. By adding the shuffle (figure 3c), in this case in the same direction on each consecutive plane, a face centered cubic structure is obtained in figure 4c. But, as shown in figure 3c, the shuffles can occur in two opposite directions. The combination of both permits to fulfill an additional condition, namely that an interface, the habit plane with a minimum of distortion is created. It turns out that this leads to a combination with approximately one shuffle from D' to D''' compensated by two from D' to D''. There is some freedom in the arrangements of the distributions. It can be on an atomic scale, by 211 211211..., or more heterogeneously by 22211111222....(1 means the shuffle from D' to D'', and 2 double that from D' to D'''). In the former case it leads to a stacking sequence of the close packed planes given by ABCBCACAB, called 9R., in the latter to a less homogeneous distribution in which 11111 or 22222 means a stacking ABCABC, called 3R, the face centered structure, and the two groups are said to be in twin orientation.. Which martensite structure actually forms depends on the more favorable energy. A consequence of the nearly zero average shuffle displacement is the small angle between the primary and the habit plane. The martensite of figure 2 has the 9R structure. The shuffle plane is visible inside one of the plates in the lower part of the figure by the contrast it creates. A third martensite structure with the stacking ABAB.. is also observed, called 2H.. It requires the shuffle sequence 121212, with no freedom to adjust for an undistorted habit plane. Thus when a thin plate advances, corresponding to that in figure 2, these shuffles alone lead to an increase in distortion energy at the growing tip, which has to be cancelled periodically by an additional displacement. This has been found to be a twin shear in the martensite on a system that reduces most efficiently the strains. It should come to no surprise that the growth of this thin plate is more difficult than for the transformation to the 3R or 9R structures.

The present description of the martensitic transformation leads to the same crystallography as the phenomenological theory. This can be seen as follows: The Bain distortion of the phenomenological model corresponds to the change from bcc to fcc, figure 4(a) to (c). It is now decomposed into the long-wave primary shear (a) to (b) and a shuffle in the same direction on each shuffle plane (b) to (c), for example from D' to D''', leading to the face centered lattice. In order to get from the face centered lattice to the required stacking sequence, shears on a certain fraction of planes have to occur from D''' to D''(figure 3c). This is the lattice invariant shear of the phenomenological theory. This large lattice invariant shear that is necessary to obtain the undistorted habit plane is now a combination of the shuffle and some primary shear

in the present description. This is a very satisfactory result since it is no longer necessary to activate a plastic deformation in the martensite by dislocation movement. Instead a small shuffle is all that is required. The shear and shuffle systems are indeed the favored ones. In addition to the low C' elastic constant the transformation proceeds from shear planes that are the favored slip planes in the bcc structure to close packed planes that are also slip planes in the fcc lattice. Therefore the atom path during the whole transformation can be considered as the most favorable one.

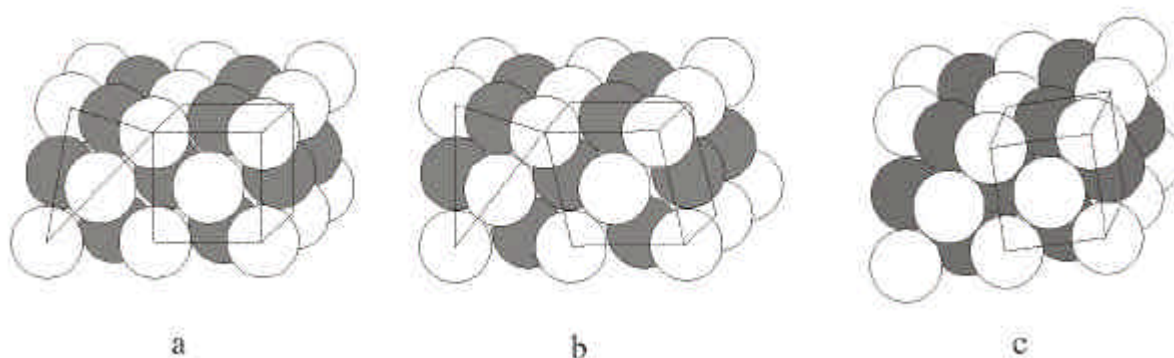


Figure 4. The transformation from B2 to 3R is illustrated by a hard sphere model. Three (110) layers of the B2 structure (a) are sheared by the same amount on each consecutive plane (b), as in figure 3b. The inclined shuffle plane marked by the triangle. The shuffle in the same direction on each plane leads to an fcc martensite (c), corresponding to $D' \rightarrow D''$ in figure 3(c).

When the sample shown in figure 2 is reheated, the martensite plates shrink in the opposite way, by a decrease in thickness and by the moving back of the thin tip, after which the original B2 structure is restored without any defects remaining. This means that the atoms move on the same path back on which they had progressed during growth. Moreover the temperature difference between their growth on cooling and their shrinking on heating is very small, of a few degrees Kelvin only. In many alloy systems a much larger hysteresis is observed that can reach several 100 K in some iron alloys. Two factors account for this different behavior. First, the thickening during growth and the shrinking during retransformation must be easy. Looking in more detail into the crystallography shows that the shuffle plane continues into a (011) plane of the β phase with little deviation, and that the close packed row in the habit plane belongs to both. Therefore the movement of the habit plane parallel to itself costs very little energy. This is different for the transformation between fcc and hex. The second component can best be discussed with reference to figure 3c. After a long-wave shear on a given primary (110) plane, the shortest shuffles correspond to those given by D' to D'' or D''' . The D'' and D''' lie in the center of the atom triangle on the plane below. In the absence of order the sites at A, A' and C are equivalent, and there would be no reason why D''' should go back to D' on retransformation, if a local stress exists that favors the movement to the center of one of the two other triangles. In the presence of the B2 order this multiplicity is no longer possible, since, as can be seen from the figure, it would lead to different order configurations. Thus it is the long-range order that forces the atoms to move back on the same path and restore the original structure without defects. This same concept works also well to rationalize the large hysteresis in other alloys when long-range order is absent. When the atoms can move back on a different path, the original atom distribution is not restored and instead a large density of defects, the dislocations, is the consequence.

As mentioned with respect to figure 1, several equivalent martensite variants can be formed if the original matrix phase has a higher symmetry than the resulting martensite, unless an external force is applied that favors one variant over the others. This leads to different arrangements of variants that have associated

with them interesting macroscopic properties with important applications. These possibilities can best be described with reference to the schematic plots of figure 5. When a single crystal of the high temperature phase is cooled without applied stress, the transformation proceeds with the formation of all martensite variants with the same probability. In the figure (a) this is indicated just by two plates of opposite shears, which keep the sample length on the average unchanged. On reheating the martensite disappears again with a small hysteresis. In the second row (b), the same initial state is used, but now a stress is applied above M_s . Although the martensite is not stable without stress that variant can be induced by the external force, which yields best to the direction of the force. This leads to a change in sample length, shown here when a compressive stress is applied. When the stress is withdrawn the crystal returns back to its original high temperature structure, it behaves as if it were some type of elastic material. It is therefore called superelastic, or pseudoelastic. When the sample is cooled below M_s without an applied stress the average length is not changed. But when a compressive stress is now applied, that variant is preferred to grow which yields best to the applied force, figure 5 (c). It will grow at the expense of the others that finally disappear. It leads to a decrease in sample length, which implies a deformation. On heating this deformation disappears and the original sample shape is restored. The crystal thus remembers its original shape even after the deformation in the martensitic state. For this reason it is called a shape memory alloy (SMA). Generally, when the crystal is cooled again after the retransformation to the matrix phase, it does not remember the previous stress induced martensitic transformation. This can be changed by a certain training, leading to the two-way shape memory effect, sketched in figure 5 (d). As a consequence the shape change can be obtained repeatedly during cooling-heating cycles without an applied stress. This possibility has important applications, and more will be said about it in a later chapter.

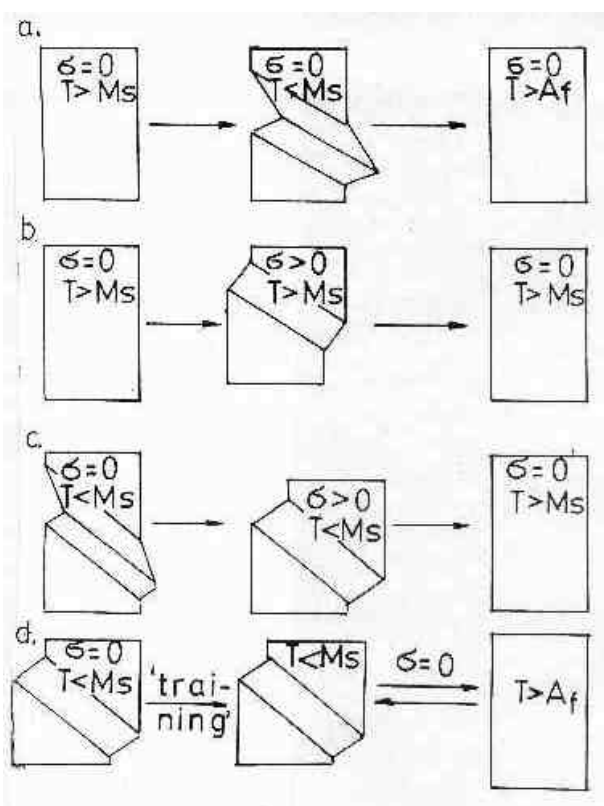


Figure 5. Illustration of the different effects associated with the martensitic transformation from a β phase single crystal, represented by the rectangle. (a): A single crystal in the β phase at temperature T above the transformation temperature M_s and without applied stress $\sigma = 0$ is cooled to $T < M_s$. All possible variant orientations appear without length change, presented here by only two variants of opposite shears. On reheating the original crystal is restored. (b): The pseudoelastic effect: A single variant orientation is induced by an applied (compressive) stress above M_s , leading to a decrease in sample length. The original length is restored on unloading. (c): The shape memory effect: A stress is applied to the polyvariant martensitic crystal after cooling without applied stress to a temperature below M_s . The growth of the most favored variant is associated with a shape change that is stable below M_s on unloading, but that disappears on heating above M_s . (d) The two-way shape memory effect (TWME): By training the shape change can be obtained during cooling-heating cycles through M_s without applied stress.

It is now appropriate to say a few words more on the way in which the different variants are accommodated on cooling without applied stress, since this is a general characteristic of the diffusionless transformations that are controlled by a large deviatoric component due to the large structural change. The

large shape change during the martensitic transformation manifests itself in a large shear at the tip of the martensite plate, as in figure 2. This means a considerable distortion of the adjacent matrix phase, which can be taken up elastically if the corresponding elastic constants are small. Another means is to create close-by another martensite variant that can compensate the shear by an opposite one. In fact the best configuration can be obtained by a group of four variants whose habit planes cluster around a $\{110\}$ pole of the matrix phase, that constitute the primary shear plane of the four. A typical distribution of martensite variants can be visualized by the observation in an optical microscope under polarized light. An example is shown in figure 6. The different variants can be discerned by the contrast they create. In this way the spontaneous transformation can proceed without the creation of internal stresses. It is even of little importance whether the whole crystal is single crystalline, or contains grain boundaries, as in the polycrystals, provided their density remains sufficiently small. Therefore the temperature M_s at the start of the transformation differs only little from that needed to finish it at M_f . A typical transformation cycle is shown in figure 7, in a plot of percentage of martensite formed as a function of temperature during cooling and heating. During heating the retransformation starts with a small hysteresis at A_s and is completed at A_f .

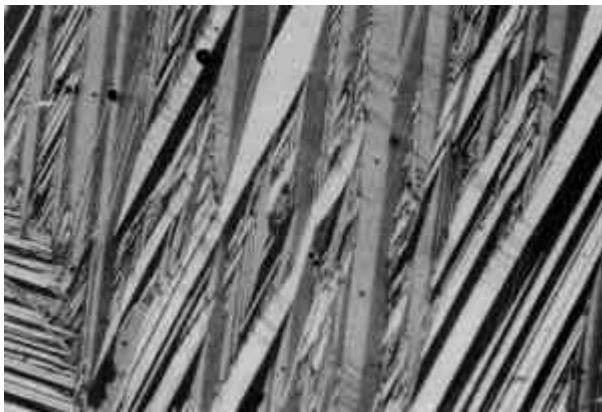


Figure 6. Characteristic surface markings associated with the martensitic transformation on cooling without applied stress. V-type configurations of martensite variants showing different contrast are visible.

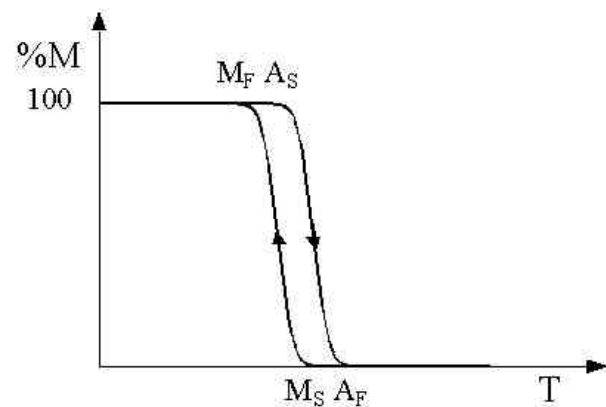


Figure 7. Temperature dependence of the percentage M of martensite formed during a cooling and heating cycle marked by the arrows. The relevant characteristic temperatures are indicated. Single crystals and polycrystals show a similar behavior.

When the martensite is induced by an applied stress, this stress field at the tip cannot be reduced but has to move across the crystal ahead of the propagating martensite plates. In a single crystal it disappears when the plate reaches the surface, whereas in a polycrystal the grain boundaries act as obstacles, and the elastic energy is deposited inside the crystal by other relaxation mechanisms. With increasing fractions of transformed material the growth of new plates gets more and more difficult due to the deposited energy. Therefore in a single crystal the transformation can proceed at a constant applied tensile force F with a sample elongation Δl , as shown in figure 8. Instead of force and length change generally the stress $\sigma = F/A$ and $\epsilon = \Delta l/l_0$ is used, with A and l_0 the initial cross section and length of the sample. In the polycrystals the stress increases continuously with the degree of transformation, instead of showing a plateau.

The stress to start the transformation in the single and in the polycrystal increases with temperature. Since the hysteresis is small, the stress σ can be considered as the sum of an equilibrium component σ_{eq} , and a frictional one σ_f , the latter being the same on loading and on unloading. The temperature dependence of σ_{eq} is described by the Clausius Clapeyron equation. This is the same equation that accounts for the

pressure dependence of the condensation temperature in gases, given in equation 1. But now the relevant parameters are no longer pressure and volume, but instead stress σ_{eq} and strain ϵ . Both can be measured, and thus the transformation entropy can be deduced.

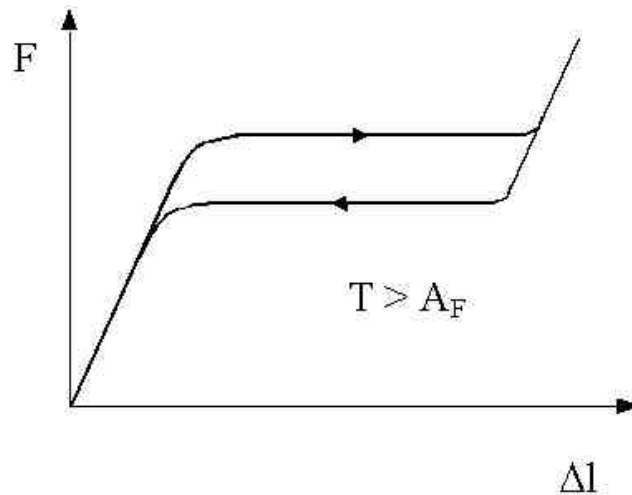


Figure 8. Relation between length change Δl and applied force F at temperature above A_F . When the transformation is complete the force increases rapidly again. This curve is typical for single crystal behavior. For polycrystals the force increases with Δl during the transformation.

The primary and shuffle systems in the noble metal alloys are favored because C' is low and the ratio of the shear elastic constants C_{44}/C' is of the order of 10. In the **Ni-Ti alloys** the martensitic transformation proceeds also from the ordered bcc to a close packed structure with little hysteresis. But in these alloys the ratio $C_{44}/C' \equiv A$ is only of a factor two. The main reason is that in the transition metals the d-electrons contribute to bonding. Their bonds are highly directional and therefore can favor the bonding to the 8 first neighbors in the bcc structure over the 12 neighbors in the close packed lattices. This contribution makes the bcc structure more stable, and increases C' . Therefore other shear systems for transformation can become favorable. A first hint can be obtained by looking for the most favorable shear constants. Apart from the C' which describes shears on $\{110\}\langle 1\bar{1}0\rangle$, the $C_{44} = C'A$ accounts for shears containing a fourfold axis, either as shear direction or as shear plane normal. For shears containing a threefold axis the relevant elastic constant is $C_1 \equiv (2C' + C_{44})/3 = C'(2+A)/3$. For $A \approx 2 C'$ and C_1 are of similar value, smaller than C_{44} . Thus a primary shear on a (112) plane in $[11\bar{1}]$ direction combined with a $(\bar{1}10)$ shuffle plane would be reasonable transformation system. This in fact has been proposed by Burgers [4] to be active for the Ti- and Zr alloys, in addition possibly to Ni-Ti [5]. The (112) and $(\bar{1}10)$ planes are common slip planes in the bcc structure. The (112) plane transforms in the resulting hexagonal martensite into a prismatic plane which is the most favored slip plane for plastic deformation in Ti and Zr with their smaller than ideal axial ratio $(c/a)_{hex}$. The $(\bar{1}10)$ shuffle plane transforms into the basal plane of the hexagonal lattice. This combination of shears permits to get to the martensite structure, but in general cannot provide an undistorted habit plane. Therefore additional twins on a different shear system have to be incorporated to reach the necessary relaxation. These twins are indeed observed in Ti, Zr and Ni-Ti. In Ni-Ti the resulting martensite is called B19'. The twinning can be avoided when the interplanar distance of the (110) shuffle planes in the matrix phase differs little from that for the close packed planes in the martensite. This indeed can be achieved by alloying. By alloying Ti with more than 32at% Ta this difference is reduced to zero and a disordered orthorhombic (distorted hexagonal) structure without twins is obtained. Similarly by

adding 7.5at% Cu to Ni-Ti it is possible to avoid twinning, resulting in B19 martensite. Whereas the Ti and Zr have no long-range order, Ni-Ti is ordered. This manifests itself also in a large hysteresis in the Ti and Zr alloys. In the ternary Ni-Ti-Cu alloys with B19 order the hysteresis is very small. In B19' Ni-Ti it is somewhat larger because of the necessity to have twins activated, as mentioned already for the formation of 2H in the Cu-Al-Zn type alloys.

In the **steels** sometimes a martensite with a (225) habit and for other steels a (259) habit is observed. The reason has been unknown till now but is easy to rationalize when the transformation from fcc to bcc is described by the combination of a long wave shear on the commonly observed close packed (111) plane with a shuffle shear on the secondary plane with the lowest elastic constant. It has been observed that in ferromagnetic Fe-alloys the C' is very low, a shuffle on a (110) plane therefore is expected and indeed leads to the observed martensite crystallography with a (259) habit. In the absence of ferromagnetism C' is high and an inclined $\{111\}$ plane becomes more favorable, leading to a habit near (225).

There is a discrepancy, however, between the predictions and the observations of the crystallography of the (225) martensite. In many publications it has been attempted to solve this puzzle. The (225) martensite brings to the attention another problem: Since the elastic constants are high, the elastic distortion energy at the tip of the growing martensite plate is high. Furthermore the calculated transformation strain is too high to be absorbed elastically by the matrix. There are several ways out. One possibility to reduce the transformation stresses is by a plastic deformation of the martensite plate, if the critical stress is sufficiently low. This occurs probably for Fe-C alloys with small amounts of C and leads to lath martensite. Another possibility is to reduce the transformation shear by an additional twin shear within the plate. This indeed is observed during the growth of the thin (225) plates, but is no longer needed once the plate has formed and only starts to thicken, because then the stress fields are no longer present and an undistorted habit plane is possible without the twins.

The iron alloys are generally disordered with a hysteresis of several hundred degrees. In the Fe-Pt alloys it is possible to introduce long-range order by the adequate heat treatment, leading to a small hysteresis and a single transformation-rettransformation path [5]. If other Fe-alloys with long-range order that are cheaper than the Fe-Pt alloys can be found that transform martensitically, it can be expected that they have shape-memory properties.

To conclude, the question listed at the beginning of the chapter can be answered in a little bit more complicated but similar terms as for the fcc to hex transformation by the activation of the most favorable transformation shear systems.

2. The martensitic transformation temperature generally depends strongly on composition. What are the factors that control the difference in the Gibbs free energy between the structures involved?

The martensitic transformation is a first order transition in the solid state, and involves a change in enthalpy and entropy. A main problem is that the differences are much smaller than the enthalpies and entropies of formation of each phase separately. This makes a quantitative evaluation in general very complex when atom rearrangements by diffusion take place. But fortunately in the shape memory alloys with the small hysteresis between the transformation and retransformation the differences can be determined experimentally with a high degree of precision. Results for the Cu-Zn-Al alloys have permitted to determine the enthalpy and entropy differences between the β phase and the martensite. The advantage of using ternary alloys is the possibility to vary the transformation temperature in a wider range than would be

possible for the binary Cu-Zn. For this reason the Cu-Zn-Al alloys have been used in the Centro Atomico Bariloche as a prototype for a better understanding of martensitic transformations in general. Another advantage is the possibility to obtain different martensite structures, depending on composition and applied stress, namely the face centered 3R with stacking sequence ABCABC, the orthorhombic 9R with ABCBCACAB stacking and the hexagonal 2H with ABAB stacking [7]. In figure 9 is plotted schematically the sequence of structures that can be obtained, starting from the disordered bcc A2-phase (all circles black), through the B2 long-range ordered β phase (black and white circles) to the 3R, 9R or 2H martensite in the binary alloy. In the ternary Cu-Zn-Al alloys a second type of $L2_1$ ordering in second neighbors can take place (black, white and gray symbols) prior to the transformation to the three possible structures, called now 6R, 18R or 2H. In the figure is shown the resulting 6R unit lattice. These structures are essentially the long-range ordered versions of the disordered equilibrium fcc, bcc and hexagonal phases that are stable at higher temperatures.

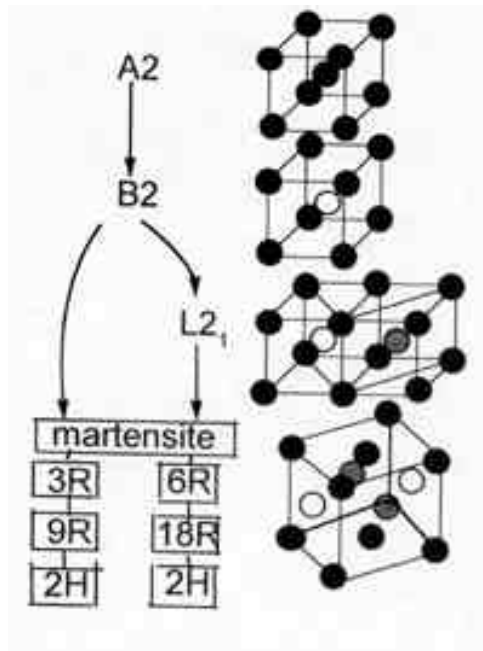


Figure 9. The different possible crystal structures obtained on cooling. The disordered A2 bcc structure orders in first neighbors to B2 (black and white sublattice sites), and ternary alloys possibly in second neighbors to $L2_1$ (black, gray and white). A half-cell in face centered tetragonal configuration is indicated. It transforms to the fcc lattice after the transformation (below). The martensite structures are different stacking sequences of close packed planes, 3R (ABC), 9R(ABCBCACAB) and 2H(AB) for inherited B2 order and 6R, 18R and 2H for inherited $L2_1$ order.

In the following only the Cu-Zn system will be discussed, since it presents already the main ingredients that are essential also in the ternary alloys. For a more detailed discussion the reader is referred to the publication [7]. The transformation occurs between a long-range ordered bcc to an fcc based structure, which differs from that between the disordered phases only by the order contribution. The disordered phases are the equilibrium fcc α and bcc β phases that are present at elevated temperatures. Thus by simply adding the long-range order contribution it should be possible to derive the Gibbs free energy for the martensitic transformation.

Long-range order generally is described in terms of pair interchange energies w_{AB}^i , which are measures of the difference in electronegativity between the atoms. They are defined for an A-B alloy as the energy difference between two A-B pairs in i -th neighbor composition compared to an A-A + B-B pair in the same i -th atom distance, $w_{AB}^i = -2V_{AB}^i + V_{AA}^i + V_{BB}^i$. When A-B pairs are favorable, w_{AB}^i is defined to be positive.

To carry out this program it is first necessary to derive the difference in Gibbs free energy between the α and β equilibrium phases, in order then to add the order contribution. The enthalpy and entropy differences are so small that they cannot be measured experimentally with the required precision. The only well determined quantity is the temperature $T_{\alpha\leq\beta}$ at which the difference in Gibbs free energy is zero, $\Delta G = \Delta H - T_{\alpha\leq\beta}\Delta S = 0$. It lies within the $\alpha+\beta$ two-phase region, more precisely in the middle of it, as can be justified. The composition dependence of this equilibrium temperature $T_{\alpha\leq\beta}$ is thus known. This is illustrated with the Cu-Zn phase diagram shown in figure 10. It is the ratio of the enthalpy difference $\Delta H_{\alpha\beta}$ and of the entropy difference $\Delta S_{\alpha\beta}$. In the Hume-Rothery noble metal alloys $\Delta H_{\alpha\beta}$ is due solely to an electronic contribution from the interaction of the Fermi surface with the Brillouin zone boundaries [8]. The configurational contribution due to the pair interchange energies determines largely the enthalpy of mixing of each phase but does not contribute to the enthalpy difference. $\Delta S_{\alpha\beta}$ results mainly from the higher vibrational entropy of the more open bcc structure, as discussed above.

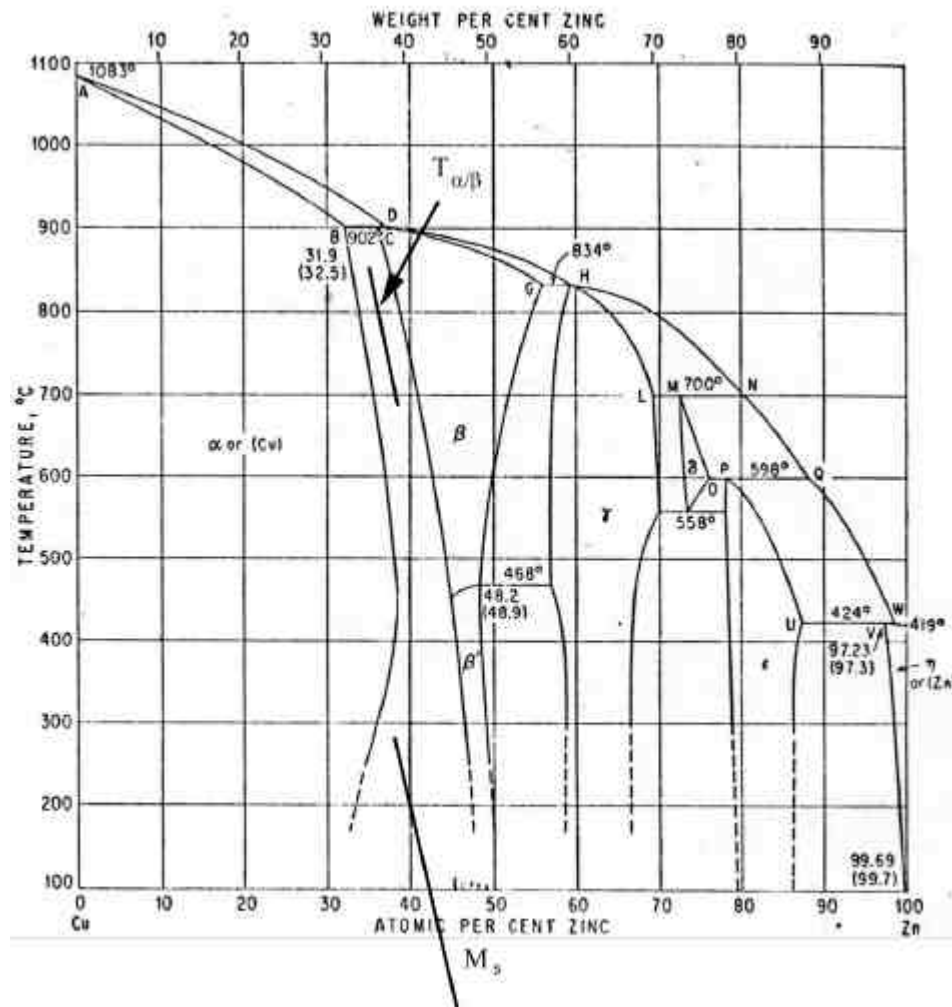


Figure 10. A Cu-Zn phase diagram. Indicated are the locations $T_{\alpha\leq\beta}$ at which the Gibbs free energies for the two equilibrium phases at elevated temperatures are the same. The composition dependence of the martensitic transformation temperature is also plotted.

To describe the martensitic transformation, only an order term has to be added to $\Delta H_{\alpha/\beta}$, whereas $\Delta S_{\alpha/\beta}$ can remain unchanged. This has been justified elsewhere [7]. $\Delta S_{\alpha/\beta}$ can be obtained from the martensitic transformation, according to the Clausius-Clapeyron equation. The long-range order contribution is obtained by summing over all pair interchange energies in the disordered and the ordered state and by taking the difference. It generally has been assumed that only the first and second neighbor pair energies are different from zero and that it is sufficient to sum only over them. This concept is not always correct, however. It has been shown experimentally [9] that up to 20-th neighbor pairs contribute, consistent with the well-established Friedel oscillations. Although the pair interchange energies have been found to decrease with increasing pair distance, the number of pairs increases, such that the product of both cannot be neglected when the total contribution to the configurational enthalpy of mixing is calculated. The reason for the existence of the Friedel oscillations is the fact that the conduction electrons are available up to the Fermi energy only, corresponding to a smallest electron wavelength. The sum of these wavelengths generally is not sufficient to screen completely the charge of the ion core at all distances, resulting in the fluctuations in the electron density as a function of distance from the atom of reference.

Fortunately, the evaluation of the order contribution in the β phase and in the martensite, which are of interest here, is easy based on the following approximation, well known from many fields of physics. In it the discontinuous distribution of atoms is replaced by a continuum above a minimum distance from the reference atom. Ordering involves only atom redistributions of about an atomic distance, which in a continuum averages out to zero when the composition and crystal structure remain constant. Below this distance the real atom distribution has to be taken into consideration. A good approximation is obtained already by including only first and second neighbor pairs. Their pair interchange energies are quite large [9] and can also be evaluated reliably from ab initio calculations [10]. Thus if the first and second neighbor pair interchange energies are known for the β phase and the martensite the order contribution to $\Delta H_{\alpha/\beta}$ can be calculated.

There is a very simple relationship between the pair interchange energies of the different structures, namely that they depend solely on the pair distance, but are independent of the crystal structure. This result is not surprising for alloy atoms whose core diameters are much smaller than the distances between the atoms, and in which the nearly free electrons provide the bonding, as has been justified by the simple pseudopotential theory [11]. This relationship is also responsible for the fact that the configurational enthalpies of mixing are the same in the α and in the β phases, although they are generally very much larger than $\Delta H_{\alpha/\beta}$.

Fortunately the martensitic transformation has several important advantages which permit to obtain reliable experimental data on which to base the evaluation. The hysteresis between transformation and retransformation is small and often is of the same order as the scatter in M_s between different samples. This permits to determine with a high degree of precision the equilibrium temperature and its stress dependence. Furthermore atom redistributions are absent due to the absence of diffusion. Therefore once the atom distribution on the lattice sites is known for the β phase, it is also known for the martensite. The ternary Cu-Zn-Al alloys are a bit more complicated, since the contribution from Cu-Zn, Cu-Al and Al-Zn pairs has to be evaluated. This has been done, and the results have permitted to understand the martensitic transformation in the Cu-Zn-Al alloys [7].

The M_s temperature in many noble metal alloys is generally far below $T_{\alpha/\beta}$ due to the long-range order, as also indicated in figure 10. This has a simple reason. In the B2 structure an atom has 8 favorable nearest neighbors, and the 6 unfavorable second neighbors at a larger distance are much weaker. In the corresponding martensite an atom has 12 nearest neighbors, but some on them are also first neighbors among themselves, which cancel partially the contribution from the center atom. In this way only 4 instead

of the 12 first neighbor pairs contribute to order. Due to this frustration effect the order energy is smaller in the martensite than in the B2 structure, and the stability range of B2 is extended to lower temperatures.

As mentioned several martensitic phases are observed, depending on composition and stress. The energy differences between 3R, 6R and 2H have been determined experimentally for the Cu-Zn-Al alloys [12]. They can be related to those of the disordered equilibrium phases at high temperatures, provided that the martensitic transformation can be described by two components as suggested here. The first is an electronic one that is determined by the electron concentration e/a , independent of the degree of long-range order, and the second a configurational one from the first and second neighbor pairs that is independent of e/a .

These types of evaluation are not only interesting for a better understanding of the stability of a large group of shape memory alloys. They also can give hints how to improve the alloy systems for a better use in technological applications. This holds in general also for other important shape memory alloys, like Ni-Ti or Ni-Al with the directional d-type bonding, which may make the evaluation more complex. Furthermore it cannot be excluded that an important contribution to the entropy difference stems from the d-type conduction electrons, since their density at the Fermi surface can be quite high.

Thus the question proposed in the beginning can be answered at least for the martensitic transformation from bcc to fcc based structures in the Cu-Zn type alloys, and most likely also in other noble metal alloys. The results can also give a hint how to treat alloys that contain transition elements.

3. What happens if after the martensitic transformation diffusion processes are permitted to occur?

This question is of considerable interest for the use in technological applications. Martensitic alloys that change their properties with time are not useful. This is one of the reasons why the Cu-Zn-Al alloys are not used extensively, in spite of being very cheap. If however the Zn is replaced by a few percent of Be [13] or Ni [14] in the Cu-Al based alloys a very different behavior is observed. The question remains still open in which way aging changes the properties and how it depends on composition and alloy system. This problem is being studied in the Centro Atómico Bariloche, and a few results shall be briefly mentioned.

During the martensitic transformation atom redistributions cannot occur. After the transformation changes can take place if in this way the Gibbs free energy can be reduced and if sufficient mobile vacancies are available for diffusion. When aging is performed at elevated temperatures a decomposition into a heterogeneous mixture of equilibrium phases is found, in agreement with the corresponding equilibrium phase diagram. This process is difficult, since it requires the nucleation of the new phases and therefore occurs only at sufficiently high temperatures. At lower temperatures, which include the range between room temperature and approximately 200°C, only atom redistributions on the lattice sites of the existing martensite structure take place. This is the range that is of most interest here since it modifies the properties in a temperature range that is used in most applications. Three different phenomena are the consequence of aging in this range:

1. The diffusion has been observed to lead to an increase in the retransformation temperature A_s to the β phase. This is called stabilization. It can have several reasons.
 - a.) If a sufficient quantity of mobile vacancies is available to redistribute the atom species on the lattice sites, a new equilibrium distribution of the atoms can be reached that minimizes the Gibbs free energy and changes the stability of the martensite with respect to the β phase.

- b.) If habit planes or nucleation sites become immobile, full-scale stabilization occurs only when these obstacles can be overcome.
 - c.) If vacancies are mobile mainly on a given sublattice, which does not favor all required atom redistributions then stabilization is reduced.
 - d.) If vacancies have annealed out or have become immobile before all required atom interchanges have taken place, then of course stabilization does not proceed to its maximum value.
2. When one martensite variant is aged it becomes more stable with respect to another variant of the same initial structure. Therefore a stress is necessary to transform the aged variant into another one, although without aging no stress would be required, apart from a friction stress. On releasing the stress the original variant is restored, unless the stress induced variant has been permitted to age for a sufficiently long time. This effect is known as “ferroelasticity”. The term is used in analogy to “ferromagnetism”, in which the orientation of a ferromagnetic domain is changed by the movement of Bloch walls in an applied magnetic field. The effect is more popularly known as rubber-like behavior, although it has nothing to do with rubber elasticity in polymers.
3. Aging in the martensite with or without additional training treatments can lead to the two-way shape memory effect.

A great deal of experimental information on the stabilization and on the ferroelasticity is available for 18R [15-21] and for 2H [22-25] Cu-Zn-Al alloys. Very high excess vacancy concentrations can be made available. Since the vacancy formation energy is low in the β phase, a large number of excess vacancies can be retained after quenching from high temperatures, up to concentrations of several 10^{-4} [26,27]. They are inherited after the martensitic transformation and accelerate diffusional processes, which are normally very slow in the close packed structures in which the vacancy formation energy is high. Obstacles to the kinetics of the transformation-retransformation cycle seem not to be important for 18R martensite, since the cycles remain smooth. The formation of 2H martensite is more difficult due to the necessity of having twins created, and the cycles are jerky even without aging. It should therefore be of no surprise if aging has an influence.

The question which types of atom redistributions occur during the stabilization has been analyzed [16]. The atom distribution in the $L2_1$ ordered β phase and that after the diffusionless transformation to the cubic 6R structure is shown in figure 9. The atom distribution with the most favorable order energy in the β phase is the following. The black sites are all occupied by Cu-atoms. Excess Cu-atoms that do not enter are statistically distributed on the grey sublattice sites, together with the Zn atoms. All Al atoms are to be found only on the sublattice sites marked by open circles. This indeed is the configuration with the most favorable order energy in the β phase, since in this way the maximum number of Cu-Al first neighbor pairs with the highest pair interchange energies are created, and since furthermore the number of favorable Cu-Zn pairs is maximized.

When a redistribution of atoms on the given lattice sites is permitted in the martensite with the inherited atom distribution, a partial disordering takes place. It does not change the Al distribution, since the ordering energy for the Cu-Al pairs is high, but leads to a homogeneous distribution of the Cu and Zn atoms on the black and grey sites. This redistribution increases the configurational entropy, but only to a smaller extent the configurational energy, such that the Gibbs free energy becomes negative and favors the reordering [16]. The corresponding β phase after the diffusionless retransformation is denoted by DO_3 . It is clear that this atom distribution has a less favorable order energy than before the aging. Whereas initially

the number of favorable Cu-Zn pairs (with Zn at the grey center and Cu at the black corners) was large, now the sites are evenly occupied with less order energy. This means that the martensite has become more stable with respect to the β phase and A_s is increased. Calculations have been performed that are consistent with this picture [16], but the expected increase in A_s is considerably larger than the observed one. Two possible reasons can be made responsible for this discrepancy. Their discussion gives some more insight into the processes that can take place in these long-range ordered phases, and therefore is thought worthwhile to be presented here.

If aging proceeds to an equilibrium distribution of the atoms then it should be independent of the quenched-in mobile vacancy concentration. Although the vacancy concentration, once present in sufficient quantities, influences the aging velocity, it should not modify the finally reached atom distribution. This implies that the final A_s temperature reached after a sufficiently long aging time is independent of the quenched-in vacancy concentration, that is, of the quenching temperature. This however is not observed, instead a strong influence of the quenching temperature on the degree of aging at a fixed temperature is observed [17]. This is surprising since it is known that a large vacancy concentration can be quenched-in, that they remain mobile and that their concentration decays much more slowly than required for equilibrium to be established [26].

A possible explanation has to do with diffusion in long-range ordered systems, in which sublattice sites with different occupation probabilities exist. Take as an example the equiatomic Cu-Zn B2 lattice (figure 3a) for illustration. A vacancy in the Cu sublattice has Zn atoms as first neighbors, and one on the Zn site has Cu as first neighbors. As a rule of thumb which often works fine, these configurations can be compared with those of a vacancy in pure Zn, and in pure Cu, respectively. Since the vacancy formation energy increases with melting temperature, a vacancy on the Cu-sublattice should have a lower formation energy than that on the Zn sublattice. Therefore in equilibrium more vacancies are expected to exist on the Cu-sublattice.

A second factor can influence the vacancy distribution in the β phase. There is some evidence that in the β phase some long-range ordering of the high quenched-in vacancy concentrations on the different sublattice occurs. This ordering is found in an equilibrium γ structure that is stable in many noble metal alloys at these same electron concentrations. It is obtained by eliminating vacancies at the center and the eight corners of a cube consisting of $3 \times 3 \times 3$ unit B2 cubes. It implies that vacancies can exist in equal amounts on the different sublattice sites. They are inherited in the martensite, in which the ordering tendency for vacancies is no longer present. Therefore they tend to favor the positions on the Cu-rich sublattice with increasing diffusion time. First neighbor jumps on the Cu rich sublattice sites are possible in the martensite (between the black sites in figure 9). Therefore it is not necessary, nor even convenient for the vacancies to interchange Cu with Zn atoms, interchanges that are required to increase stabilization. Stabilization thus proceeds to lower A_s temperatures than expected for equilibrium [17,18].

A second possibility to account for the observed changes in A_s temperature will now be discussed on the basis of results obtained from the stabilization of the 2H martensite in Cu-Zn-Al alloys with a high electron concentration of $e/a = 1.53$. At this e/a the 2H structure is the most stable one, but 18R and 6R can be induced by an applied stress. It has been observed that sometimes stabilization leads to an increase of less than 100 K in the A_s temperature, as commonly observed for 18R. Sometimes increases by about 300 K are found that agree better with the calculated changes of A_s [22] This has been a puzzle. Recent experiments have been performed to resolve this strange behavior [23-25]. Since it involves another

property of long-range ordered lattices that have previously not been mentioned, a more detailed description is added.

To simplify the discussion consider the 2H structure as a basic face centered one into which stacking faults are introduced regularly on each second close packed plane. This is not completely correct since the regularly spaced faults are the elements of a new structure, but it is a good approximation if long-range order energies are described in terms of first and second neighbor pair interchange energies, since they are not modified by the introduction of a fault. Thus in the following the order in the face centered lattice will be analyzed, with 2H in mind.

The changes during the martensitic transformation prior to the aging can be decomposed into two components in the Gibbs free energy. A decrease due to the collapse of the high amplitude vibrational modes in the β phase, combined with an increase in energy associated with the less favorable order energy in the martensite due to the frustration effect, as mentioned before. The frustration increases with distortion towards the fcc lattice, because the unfavorable second neighbor pairs in the β phase become first neighbors. It should therefore not come to a surprise that the martensite structure prefers not to be distorted to the fully cubic fcc lattice, but to remain at an intermediate state of distortion, when the free energy gain is offset by the energy increase from the frustration effect. This intermediate structure between bcc and fcc can be described by a basic face centered tetragonal lattice. It can be characterized by a ratio $(c/a)_{\text{fcc}} \equiv \psi$ of the unit tetragonal cell. For the fcc lattice it is $\psi = 1$, for the original bcc structure in terms of a tetragonal unit $\psi = 1/\sqrt{2}$ (compare with figure 9). The lattice parameters for 18R and 2H have been measured by X-ray analysis, and indeed ψ has been found to remain intermediate between bcc and fcc, namely $\psi = 0.92$ [19,20].

During aging two things happen. The more disorderly redistribution of the atoms on the three sublattice sites means an increase in configurational entropy and thus favors the stabilization, but again the frustration effect would like to keep it somewhat distorted. As a result aging proceeds until the decrease in Gibbs free energy due to reordering is compensated by the increase in the frustration at another intermediate ψ . This is what happens in 18R and in 2H and leads to only small increases in A_s . This unfavorable contribution can be overcome. At a critical applied stress this distortion becomes unstable, and if no other contributions were present the change to $\psi = 1$ could take place at this constant stress. But, as in disordered alloys, an elastic deformation leads to an increase in stress and elastic energy. This is illustrated in figure 11. When a tensile stress is applied to a 2H single crystal, at a critical stress a change in slope is present. It overcomes the unfavorable component, but due to the elastic distortion the stress increases on further deformation. When the sample is unloaded without aging the same curve is traced backwards without hysteresis. It can thus be considered as a transformation to a new phase with different lattice parameters and a different free energy, a transformation in which dissipation of energy is absent since it occurs without hysteresis. When the sample is aged at a constant stress that overcomes the unfavorable distortion and keeps the elastic energy constant, then the stabilization can proceed to the final $\psi = 1$ and a higher A_s . The Gibbs free energy decreases and the strain ϵ , i.e. the sample length increases, as shown in figure 11. The stabilization velocity decreases with increasing aging time, as seen from the insert. After unloading the strain is retained, and the total strain of 3% in this sample is in close agreement with what would be expected for a change in ψ from 0.92 to 1.

The difference between the weak and strong increase in A_s on aging therefore can be related to the possibility to overcome the unfavorable frustration effect by an applied stress. In 18R martensite this critical stress is apparently much higher and is not reached. Therefore stabilization has been observed to

proceed only to smaller increases in A_s . In 6R, on the other hand a ψ close to 1 is observed without the need to age under stress [19,20]. These differences for the different martensite structures strongly suggest that an electronic factor from the conduction electrons and their interaction with the Fermi surface may play a role.

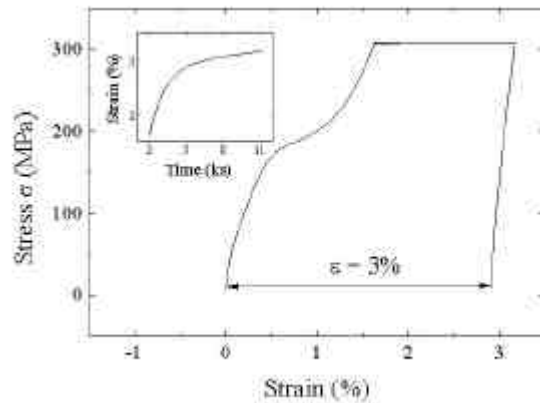


Figure 11. Length changes observed during stress inducing a 2H Cu-Zn-Al single crystal. First decrease in slope is associated with the formation of an intermediate structure that shows no hysteresis between the loading-unloading cycle. Aging at constant stress leads to an increase in sample length, i.e. strain, that slows down with aging time (inset) and that is retained after unloading.

Thus as shown the processes that occur during the diffusion in the Cu-Zn-Al martensites are not only important to improve their use in the technological applications, but show interesting basic aspects, many of which are expected to be present also in other long-range ordered structures and in shape memory alloys. A further great advantage of these studies is the possibility to start with a well-defined initial configuration, namely that obtained right after the martensitic transformation from a completely characterized matrix phase.

4. How can the properties of shape memory alloys be improved by thermomechanical treatments?

There is an ample spectrum of possibilities to modify the martensitic transformation in shape memory alloys by thermomechanical treatments. These modifications are often essential to obtain materials with the required properties for technological applications. Although the study of single crystals permits to separate and analyze the parameters that determine the behavior of the shape memory alloys, in technological applications nearly exclusively polycrystals are used. It is well known that many properties of materials can be changed by the manipulation of the grain structure. In the following only a few examples will be given for polycrystalline Cu-Zn-Al alloys and for the widely used Ni-Ti polycrystals. These examples are selected because they are considered to be useful to improve the required technological applications in many different alloys.

First example: Training methods to obtain the two-way shape memory effect (TWME) in 18R Cu-Zn-Al alloys. An often used training method is to cycle the alloy repeatedly through the martensitic transformation at a fixed applied stress, or to stress induce repeatedly above the spontaneous transformation temperature. In single crystals a large number of cycles is necessary to create some defects that could act as favorable sites for the growth of the preferred martensite variants. In the polycrystals the strain field of the growing martensite plates interacts strongly with the grain boundaries and leads to relaxed configurations

that depend on the orientation of the initial variant [28]. Thus it can be expected that these configurations can act as nucleation sites for the variant that has the same orientation as the original one, even without a further applied stress.

An alternative is to stabilize the relaxed configurations by aging the martensite at an applied stress. After aging and unloading the retained martensite starts to retransform at a higher A_s temperature due to stabilization, but once retransformed to the β phase all aging effects anneal out fast, and the lower transformation temperatures corresponding to the unaged sample are restored. Thus the procedure to obtain the TWME by aging is the following. After the stabilization at an applied stress the induced martensite variant is heated to a temperature between A_s and A_f , during which a part retransforms to the β phase, and the other part is retained. The latter can serve as nuclei when the sample is cycled subsequently through the martensitic transformation at the lower temperatures without an applied stress. If the maximum temperature remains close to A_s then the fraction that has retransformed and can become responsible for a TWME is small, if a temperature close to A_f is reached the density of possible nuclei for a TWME is small and may not be sufficient to induce the TWME. It is clear that in single crystals it is difficult to control the correct temperature up to which the sample should be heated, since the difference between A_s and A_f is small [29]. In polycrystals the difference between A_s and A_f increases with decreasing grain size, and a TWME can be much better controlled, an important aspect for technological applications [30].

In applications it is desired to use the alloy as a smart material that senses a temperature change and can act as a switch against an opposing force, a spring, for example. For this reason it is also important to know how much work can be done against an opposing force. Some results have been published [30, 31]. It should be clear that the aging after stress inducing the martensite is a simpler and less costly method than the repeated cycling through the transformation. A good alternative is also to combine the two processes, but this depends on the properties that are desired.

Second example: The influence of precipitates. The alloys that transform martensitically are generally only metastable and decompose on slow cooling by the formation of precipitates. The precipitates that most easily and rapidly grow are coherent and produce coherency stresses around them which influence the formation of the martensite variants. In the Cu-Zn-Al alloys the cubic γ phase precipitates are most easily formed. Their presence modifies the martensitic transformation, as has been amply analyzed [28].

The influence of coherent precipitates manifests itself spectacularly in the Ni-Ti alloys [32]. In alloys with more than 50.5 at% Ni coherent plates of Ti_3Ni_4 form easily on aging between 300 and 500°C. They produce an anisotropic stress field. If during the precipitation an external stress is applied, only the most favorable orientations grow. Their presence leads to the formation of selected martensite variants on cooling and is associated with a shape change. This TWME has been called the all-round shape memory effect.

Third example: Superelasticity in Ni-Ti polycrystals. Whereas in single crystals the martensite can be fully induced at a constant stress, in polycrystals the stress has to be increased continuously, as discussed above. For many applications such a variation is not acceptable. By an adequate thermomechanical treatment it is possible to induce the transformation at constant stress also in polycrystals. An example are the nearly equiatomic Ni-Ti alloys [32] with an M_s temperature between about +70 and -70°C. The treatment that is applied to improve the degree of pseudoelasticity is to deform the material heavily, for example by cold rolling. By subsequently annealing at 400°C below the recrystallization temperature of about 600°C a very complex structure is created consisting of dislocations and small twinned martensite variants. The resulting stress-strain cycle looks very similar to that for the single crystals, figure 8. The

large-scale application of the Ni-Ti shape memory alloys is predominantly due to this effect.

5. For what applications are shape memory alloys useful?

The Ni-Ti based shape memory alloys have found widespread applications in medicine, due to their compatibility with the living organism. Different shape memory alloys are also being used for many technological applications, in some cases opening up new fields of application, in others improving the performance compared to the more traditional materials. In the following a few examples will be listed in order to show that the shape memory alloys are not only interesting from a scientific point of view, but are also new materials that have found already - and continue to do so - uses in our modern material world.

First example: Medical applications [33,34]. The Ni-Ti 'nitinol' materials are nowadays widely used to straighten out irregularly grown teeth, or a bent column by using the pseudoelastic behavior. As mentioned above, by the thermomechanical treatment the desired properties can be obtained, namely full pseudoelasticity and a constant transformation and retransformation stress, independent of the amount of transformation. Traditionally stainless steels had been used, but their disadvantage is that they behave elastically, with a strong decrease in stress with a decrease in strain. Therefore they have to be adjusted frequently with the decrease in distortion.

Other important applications are the stents, devices that are used to expand diseased and constricted vessels and arteries [34]. They can be inserted in the pseudoelastic state, constrained by a surrounding flexible tube which is pulled off when the stent is located at the desired site and expands to the final diameter. An alternative is to introduce a stent in the compressed martensitic state at a lower temperature letting it expand when reaching the body temperature. One important problem is fatigue. The pressure at a stent installed in an artery varies periodically with the heartbeat of about one cycle per second producing repeated deformation cycles. They result in what is called internal friction, and are responsible for the fatigue cracks that may appear after a long useful life. Traditionally, as an alternative stents of stainless steels are used. After insertion they have to be expanded by plastic deformation which is achieved by inflating a balloon from the inside.

Second example: Nonmedical applications [33,35].

There are many nonmedical applications, and good summaries can be found in the literature. Some items are produced because they increase the comfort, as eye glass frames and the headband of headphones. Their pseudoelastic behavior guarantees that they exert a constant pleasant pressure at the head.

Couplings made of shape memory alloys have some definite advantages over the more traditional soldering. Rings of this material are cooled into the martensite phase, then are expanded. In this shape they are slipped over the tube ends which are to be connected. After warming up they retransform to the original smaller diameter. As an alternative alloys with a higher transformation-retransformation hysteresis have been developed that can be deformed in the martensitic state at room temperature. They retransform to the original shape only after heating and remain in this shape after cooling to room temperature due to the large hysteresis.

Microactuators have been developed in which a shape memory element changes its shape against an opposing force when the temperature is changed. The opposing force can be a spring that deforms the element at low temperatures in the martensitic state, but is too weak to prevent the original length from being restored on heating.

A great deal of activity is devoted to use the shape memory alloys as smart materials. When they sense an undesired change in temperature they change their shape on passing through the martensitic transformation temperature. This permits to activate a control system that cancels the temperature change, or takes other means to avoid damages. In this way the correct temperature for 'mate tea' can be guaranteed by cutting the electrical contact when the water gets too hot. Many other applications as smart devices have been developed. Here the important parameters are a small hysteresis and the absence of aging.

An important application is the use as shock absorbers, especially during earthquakes. The seismic energy is transferred to the material, it is absorbed associated with a shape change and the absorber returns back to its original shape after the wave has decayed. One problem is that the device has to work at any time when an earthquake takes place, in winter and in summer. Unfortunately the stress to induce the martensitic transformation depends on temperature, according to the Clausius-Clapeyron relationship, being especially strong in the Ni-Ti alloys. Therefore it is attempted to develop alloys which show a weak temperature dependence of the transformation stress. They also must have a high dissipation potential and have to return back to the original state afterwards and must not change its properties with time. An important group of shape memory alloys that are studied extensively are the ferromagnetic ones. In these alloys it is attempted to induce a shape change by applying a magnetic field instead of a mechanical stress or a change of temperature. To them belong the Heusler alloys of composition A_2BC and $L2_2$ order at elevated temperatures. The Cu_2AlMn alloy is ferromagnetically ordered up to a Curie temperature of $560^\circ C$. Unfortunately the β phase remains stable down to the lowest temperatures. In order to have a martensitic transformation it is necessary to reduce the Mn content in this alloy system. But this leads also to a decrease in the Curie temperature [36]. Other alloys that are ferromagnetic and transform martensitically are the Heusler alloys with compositions around Ni-25%Ga-25%Mn. Their study constitutes one of the most active fields of research [33,37-39]. In them shape changes can be induced by magnetic fields and are much larger than the commonly used magnetostrictive compounds, as terfenol-D, the ternary $Tb_xDy_{1-x}Fe_2$ with x around 0.27 [40]. When a magnetic field is applied the spins reorient themselves parallel to the field with the least possible magnetic anisotropy and energy dissipation, thus increasing the magnetization, and simultaneously increasing the sample length due to the magnetostriction.

In the shape memory Ni-Ga-Mn alloys a behavior similar to that for the magnetostrictive compounds is observed, but with a strain of one order of magnitude higher than in terfenol-D. In this case the reason is different. As mentioned before in the common shape memory alloys the most favorably oriented martensite variants can grow at the expense of others when a stress is applied. This leads to a shape change. In the present magnetic alloys it is necessary to have a high magnetic anisotropy, in order to have the spin orientations coupled with the crystal orientation. When a magnetic field is now applied the spins would like to reorient themselves, but due to the high anisotropy cannot do so. The only means to reduce the magnetic energy is to have the martensite variant grow that has the highest spin component parallel to the applied magnetic field. The hysteresis in this case is due to the friction during the movement of the interfaces between the martensite variants.

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