# Three-dimensional Landau theory describing the martensitic phase transformation of shape-memory alloys

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**Abstract.** In shape-memory alloys a first-order martensitic phase transition is responsible for pseudo-elastic and for ferro-elastic stress–strain relations. To describe this behaviour a modified Landau theory is proposed in which the free energy of the crystal depends on the temperature and on the full strain tensor. The energy is invariant with respect to the cubic point group $O_h$ of the high-temperature phase. To predict the cubic-to-monoclinic phase transition of $\beta$-phase shape-memory alloys an expansion up to sixth order in strain is necessary for which, for the class of alloys considered, odd terms may be neglected. For a CuAlNi alloy the expansion coefficients are determined by comparison with experimental results. In contrast to classical Landau theory of second-order phase transitions, not only a single second-order but also a fourth-order expansion coefficient depend on temperature.

## 1. Introduction

The shape-memory effect in certain metallic systems called 'shape-memory' alloys has been the subject of considerable experimental effort. In some temperature ranges these alloys show pseudo-elastic and ferro-elastic stress–strain curves. It transpires that these peculiarities are the consequence of a first-order martensitic phase transition which is connected with a nearly-volume-conserving spontaneous deformation of the crystal lattice (Delaey *et al* 1974). In addition to temperature, external stress may induce the phase transition from the high-temperature austenitic phase to the low-temperature martensitic phase. At low temperature stress causes deformation twinning between crystallographically equivalent martensite variants.

In spite of some interesting applications of these alloys, up to now there has been no conclusive theoretical description of their mechanical or thermomechanical behaviour. We propose here to use a modified Landau theory to derive a free-energy function dependent on strain and on temperature which, as a thermodynamic potential, enables calculation of the equilibrium properties. For some alloys there have been attempts in this direction. Nittono and Koyama (1982) and Koyama and Nittono (1982) derived a free-energy function for indium alloys such as InTl, InCd, InPb and InSn undergoing a cubic-to-orthorhombic or cubic-to-tetragonal phase transition. Group theory was used in order to guarantee the correct symmetry of the free energy. Later on Barsch and

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Krumhansl (1984) included strain-gradient terms to calculate the structure of moving twin boundaries between tetragonal martensite variants in InTl. NiTi or copper-based shape-memory alloys, which are more important for applications, undergo a cubic-to-monoclinic phase transition. Within a one-dimensional model Falk (1980) proposed a free-energy expansion of sixth order in a single shear strain component. An expansion up to fourth order in the full strain tensor invariant with respect to the cubic group has been given by Liakos and Saunders (1982). As will be seen below, for shape-memory alloys an expansion up to sixth order is necessary. It is the aim of this paper to construct such a free-energy function invariant with respect to the cubic symmetry group $O_h$ of the high-temperature phase describing the first-order phase transition to monoclinic martensite. The expansion coefficients are determined for a CuAlNi alloy. Furthermore the stress–strain relations and the heat of transformation are derived and compared with experiments.

## 2. The martensitic phase transition in shape-memory alloys

Before constructing the free-energy function some remarks on the martensitic phase transition in shape-memory alloys are appropriate. In this section we deal with the temperature-induced transition, i.e. both the phases are assumed to be in a stress-free state. In NiTi or copper-based alloys such as CuZn, CuAlNi, CuAlZn and CuAlGa and other $\beta$-phase alloys such as NiAl, AuCd and AgCd, the austenite shows, at temperatures not much above the martensitic transition temperature, an ordered BCC structure of point group $O_h$(m3m). The space groups differ in the various alloys but they are not relevant for the symmetry of the strain tensor.

When austenite transforms to martensite on cooling a spontaneous strain appears. On the scale of the lattice cell of austenite, that is over a few ångstrom, the Bain strain deforms the cubic unit cell to an orthorhombic one. As a consequence the following misfit problem arises. Imagine an inclusion of orthorhombic martensite in a cubic austenitic matrix. Even if there is no volume change then across the interface between both the phases a lattice misfit occurs leading to a long-range stress field of high energy. One way of reducing this stress is to build an incoherent interface, i.e. an amorphous boundary layer. This is not the way shape-memory alloys solve the problem since it is observed that the phase transition proceeds by rather rapid interface motion which is possible only for coherent interfaces. The only possibility of vanishing lattice misfit stress across a coherent interface occurs if it is invariant with respect to the strain. This means that any material vector in the interface must not be deformed. In order that an invariant plane exists at least one eigenvalue of the strain tensor has to vanish. In addition, the remaining two eigenvalues must be of opposite sign. However, the orthorhombic Bain strain does not fulfil this condition. As a consequence, in shape-memory alloys martensite forms as an internally microtwinned or faulted phase, that is, layers of twins of orthorhombic martensite alternate on a scale of a few atomic distances. In the alloys mentioned the twinning or basal plane is {110} if referred to cubic axes. The relative amount of twins is such that the total strain resulting from Bain and microtwinning strain does not deform the so called habit plane which therefore acts as the contact plane between the austenite and martensite. The orientation of twinning and habit plane, the Bain strain, the total strain and the amount of twins are related by WLR theory (Wechsler et al 1953). A review on this topic is given in the book by Wayman (1964).

In the shape-memory alloys mentioned the microtwinning occurs in a regular pattern

on a scale of a few cubic unit cells, so that a monoclinic lattice containing many atoms per unit cell results forming a martensite variant. Typically, those variants show a 2H, 3R, 9R or 18R structure, depending on the alloy under consideration. On a length scale roughly four orders of magnitude bigger it is observed by light microscopy that shape-memory alloys form a macrotwinned structure in the martensite state. This is because a plate-like inclusion of martensite variant in an austenite matrix generates, due to a shape misfit, a stress field at its circumference even if there is no lattice misfit across the habit plane. This stress field decreases almost to zero if an arrangement of twins of monoclinic martensite variants forms (self-accommodating groups: see, e.g., Tas *et al* (1973) and de Vos *et al* (1978)).

The free-energy function to be constructed in the present paper deals with the deformation of single crystals on a scale between the monoclinic lattice and the self-accommodating groups. The appropriate strain is therefore defined on a scale of a few nanometres. As a consequence the Bain strain is below the resolution of the theory and does not occur here. On the other hand the deformation of a macroscopic sample consisting of self-accommodating groups of martensite is not dealt with either. Instead the theory describes the phase-transition phenomena between cubic austenite single crystals and monoclinic single-crystalline martensite variants on a mesoscale. In order to describe the macroscopic behaviour of shape-memory alloys one could proceed by some averaging over the different martensite variants forming the macroscopic sample in the way sketched by Falk (1989) for a one-dimensional model. However, this is not the objective of the present paper.

To define mathematically the appropriate mesoscale strain measure consider a triad of materially fixed vectors $a^i$ which in stress-free austenite are chosen to be orthogonal and of the same mesoscale length $a_0$ of a few nm. For simplicity take vectors parallel to the cubic axes. As a result of deformation which may be due to the martensitic phase transition or to an applied load the vectors change to $\bar{a}^i$. The symmetric strain tensor is defined by

$$e_{ij} = \tfrac{1}{2}(\bar{a}^i \cdot \bar{a}^j - a^i \cdot a^j)/a_0^2 = \tfrac{1}{2}(\bar{a}^i \cdot \bar{a}^j/a_0^2 - \delta^{ij}). \tag{1}$$

The product phase on the mesoscale is called a martensite variant. In the shape-memory alloys mentioned, a martensite variant shows monoclinic symmetry of point group $C_2(2)$ whereas the space groups are different for the various alloys. Since the order of the cubic symmetry group $O_h$ of the parent phase is 48 and that of the monoclinic group $C_2$ of the product phase is two, 24 possible orientations of the product occur, i.e. there exist 24 martensite variants. All of them follow from a single one by applying symmetry operations of the cubic group. Since they are equivalent crystallographically their energies coincide.

## 3. Free-energy expansion

The equilibrium properties of a system are determined by the free-energy function. In Landau's theory of second-order phase transitions one restricts the variables on which $F$ depends to the temperature and to the so called order parameter which characterises the difference between the phases. Furthermore, it is argued that the order parameter transforms as one of the irreducible representations (IRs) of the more symmetric high-temperature phase (Landau and Lifshitz 1980). In order to describe not only the first-order martensitic phase transition but the complete thermomechanical behaviour of the

system, one has to take into account the full strain tensor. The dependence of $F$ on strain is governed by the point group $O_h$ of the high-temperature phase. If a symmetry operation in three-dimensional space is represented by the $3 \times 3$ matrix $\mathbf{D}$ with components $D_{ij}$ with respect to the cubic orthogonal base vectors $a^i$, then the strain matrix or strain tensor transforms according to

$$e'_{ij} = D_{im}D_{jn}e_{mn}$$
$$\mathbf{e}' = \mathbf{D}\mathbf{e}\mathbf{D}^\mathsf{T}.$$

(2)

Symmetry requires that

$$F(\mathbf{e}, T) = F(\mathbf{e}', T)$$

(3)

for each of the 48 matrices $\mathbf{D}$. Necessary group-theoretical tools for exploiting the symmetry requirements are found in Lyubarsky (1960). For the purpose of generating symmetry-adapted free-energy functions it is more convenient to look at the symmetric strain tensor as a vector in a six-dimensional strain space $S$ spanned by the dyads

$$\varphi_1 = a_1 \otimes a_1 \qquad \varphi_2 = a_2 \otimes a_2 \qquad \varphi_3 = a_3 \otimes a_3$$
$$2\varphi_4 = a_2 \otimes a_3 + a_3 \otimes a_2$$
$$2\varphi_5 = a_1 \otimes a_3 + a_3 \otimes a_1$$
$$2\varphi_6 = a_1 \otimes a_2 + a_2 \otimes a_1.$$

(4)

The components of strain with respect to $\varphi_K$ ($K = 1 \ldots 6$) are denoted by $e_K$:

$$e_1 = e_{11} \qquad e_2 = e_{22} \qquad e_3 = e_{33}$$
$$e_4 = 2e_{23} \qquad e_5 = 2e_{13} \qquad e_6 = 2e_{12}$$

(5)

describing the strain in Voigt notation. In strain space $S$ spanned by $\varphi_K$, symmetry operations of the group $O_h$ are represented by the $6 \times 6$ matrices $d_{KL}$ following from the representation $D_{mn}$ so that the strain transforms according to

$$e'_K = d_{KL}e_L.$$

(6)

The representation $d_{KL}$ of group $O_h$ is reducible into the IRS $\Gamma_1$, $\Gamma_{12}$ and $\Gamma_{25'}$. Accordingly the strain space $S$ decomposes into the invariant subspaces $S_1$ (one-dimensional), $S_{12}$ (two-dimensional) and $S_{25}$ (three-dimensional):

$$S = S_1 \oplus S_{12} \oplus S_{25}$$

(7)

which are spanned by $\Phi_{\bar{K}}$ ($\bar{K} = 1 \ldots 6$):

$$
\begin{aligned}
S_1 &\qquad \Phi_{\bar{1}} = \varphi_1 + \varphi_2 + \varphi_3 \\
S_{12} &\qquad \Phi_{\bar{2}} = 2\varphi_3 - \varphi_1 - \varphi_2 \qquad \Phi_{\bar{3}} = \varphi_1 - \varphi_2 \\
S_{25} &\qquad \Phi_{\bar{4}} = 2\varphi_4 \qquad \Phi_{\bar{5}} = 2\Phi_5 \qquad \Phi_{\bar{6}} = 2\varphi_6.
\end{aligned}
$$

(8)

If referred to the symmetry-adapted base vectors $\Phi_{\bar{K}}$, the components of strain are denoted by $e_{\bar{K}}$.

$$e_{\bar{1}} = (e_1 + e_2 + e_3)/3 = \mathrm{tr}(e_{ij})/3$$

(9)

in the linear approximation describes the volume change during deformation.

$$e_{\bar{2}} = (2e_3 - e_1 - e_2)/6 = (2e_{33} - e_{11} - e_{22})/6$$
$$e_{\bar{3}} = (e_1 - e_2)/2 = (e_{11} - e_{22})/2 \tag{10}$$

represent shear deformations on the {110} planes in the $\langle\bar{1}10\rangle$ directions. The remaining components

$$e_{\bar{4}} = e_4/2 = e_{23} \qquad e_{\bar{5}} = e_5/2 = e_{13} \qquad e_{\bar{6}} = e_6/2 = e_{12} \tag{11}$$

denote shear deformations on the {100} planes in the $\langle 010 \rangle$ directions.

As in Landau theory it is assumed that the free energy is an analytic function so that it can be expanded into a power series with respect to strain:

$$F(\mathbf{e}, T) = F^0(T) + F^1(\mathbf{e}, T) + F^2(\mathbf{e}, T) + \ldots \tag{12}$$

with $F^n$ an expression of the $n$th degree:

$$F^n(\mathbf{e}, T) = C^{L_1 \cdots L_n}(T)e_{L_1} \cdots e_{L_n} \qquad L_j = 1 \ldots 6, n \geq 1. \tag{13}$$

Here and in the following the Einstein convention is used, i.e. over indices occurring twice summation is implied. Each $F^n$ has to meet the symmetry requirements (3) and (6) individually. The expressions (13) can be interpreted as scalar products of two vectors, namely $C$ and $\mathbf{e} \otimes \ldots \otimes \mathbf{e}$, both elements of a symmetrised product space $S_{\text{sym}}^n$ spanned by the symmetrical $n$-fold tensorial products

$$(\varphi_{L_1} \otimes \ldots \otimes \varphi_{L_n})_{\text{sym}} = \varphi_{L_1} v \ldots v \varphi_{L_n} \qquad 1 \leq L_1 \leq L_2 \leq \ldots \leq L_n \leq 6. \tag{14}$$

The symmetry requirement on $F^n(e, T)$ explicitly reads

$$C^{L_1 \cdots L_n}e_{L_1} \cdots e_{L_n} = C^{L_1 \cdots L_n}d_{L_1 M_1} \cdots d_{L_n M_n}e_{M_1} \cdots e_{M_n} \tag{15}$$

and is valid for arbitrary strain $e$ and every symmetry operation $d$ of group $O_h$. Therefore it follows that

$$C^{L_1 \cdots L_n} = d_{L_1 M_1} \cdots d_{L_n M_n}C^{M_1 \cdots M_n}. \tag{16}$$

The products $d_{L_1 M_1} \cdots d_{L_n M_n}$ generate a representation $d_{\text{sym}}^n$ of the group $O_h$ acting on space $S_{\text{sym}}^n$ which, in general, is reducible even if the representation generated by $d_{LM}$ in space $S$ is irreducible. Equation (16) says that the coefficients $C$ in order to obey symmetry have to be built up by invariant directions $n_j$ of space $S_{\text{sym}}^n$ according to

$$C^{L_1 \cdots L_n} = \sum_{j=1}^{j^n} F_j^n \eta_j^{L_1 \cdots L_n} \tag{17}$$

where the sum goes over all the invariant directions. $F_j^n$ are independent material parameters of $n$th order. As invariants, the $n_j$ transform according to the identical representation of $O_h$. There are as many invariant directions as the identical representation occurs in the decomposition of the representation $d_{\text{sym}}^n$ into IRs. This number is given by

$$j^n = \frac{1}{g} \sum_{i=1}^{g} \text{tr}(d_{\text{sym}}^n(i)) \tag{18}$$

where $d_{\text{sym}}^n(i)$ is the matrix of group element number $i$ in the representation $d_{\text{sym}}^n$. $i$ runs over all the group elements, that is from 1 to group order $g$ which is 48 for group $O_h$. The

**Table 1.** Strain invariants $J_j^n$ of first and up to fourth order of the cubic group $O_h$. Strain components in symmetry-adapted coordinates (equations (9)–(11)).

| Invariant | | Strain space |
|---|---|---|
| $J_1^1$ | $e_1$ | $S_1$ |
| $J_1^2$ | $(J_1^1)^2$ | $S_1$ |
| $J_2^2$ | $3e_2^2 + e_3^2$ | $S_{12}$ |
| $J_3^2$ | $e_4^2 + e_5^2 + e_6^2$ | $S_{25}$ |
| $J_1^3$ | $(J_1^1)^3$ | $S_1$ |
| $J_2^3$ | $J_1^1 J_2^2$ | $S_1 \oplus S_{12}$ |
| $J_3^3$ | $e_2(e_2^2 - e_3^2)$ | $S_{12}$ |
| $J_4^3$ | $e_4^2(e_3 - e_2) - e_5^2(e_2 + e_3) + 2e_6^2 e_2$ | $S_{12} \oplus S_{25}$ |
| $J_5^3$ | $J_3^1 J_3^2$ | $S_1 \oplus S_{25}$ |
| $J_6^3$ | $e_4 e_5 e_6$ | $S_{25}$ |
| $J_1^4$ | $(J_2^2)^2$ | $S_{12}$ |
| $J_2^4$ | $e_4^4 + e_5^4 + e_6^4$ | $S_{25}$ |
| $J_3^4$ | $(J_3^2)^2$ | $S_{25}$ |
| $J_4^4$ | $J_2^2 J_3^2$ | $S_{12} \oplus S_{25}$ |
| $J_5^4$ | $e_4^2(e_2 - e_3)^2 + e_5^2(e_2 + e_3)^2 + 4e_6^2 e_2^2$ | $S_{12} \oplus S_{25}$ |
| $J_6^4$ | $(J_1^1)^4$ | $S_1$ |
| $J_7^4$ | $(J_1^1)^2 J_2^2$ | $S_1 \oplus S_{12}$ |
| $J_8^4$ | $J_1^1 J_3^3$ | $S_1 \oplus S_{12}$ |
| $J_9^4$ | $(J_1^1)^2 J_3^2$ | $S_1 \oplus S_{12}$ |
| $J_{10}^4$ | $J_1^1 J_4^3$ | $S_1 \oplus S_{12} \oplus S_{25}$ |
| $J_{11}^4$ | $J_1^1 J_6^3$ | $S_1 \oplus S_{25}$ |

invariant directions $\eta_j$ can be calculated by Wigner projection operators according to

$$\eta_j^{M_1 \cdots M_n} = \sum_{i=1}^{g} d_{L_1 M_1}(i) \ldots d_{L_n M_n}(i)\varphi_{L_1}v \ldots v\varphi_{L_n} \tag{19}$$

where $d_{L_1 M_1}(i)$ is the representation matrix of group element number $i$ in strain space $S$. To get all the invariant directions one has to insert the different base vectors $\varphi_{L_1}v \ldots v\varphi_{L_n}$ $(1 \leq L_1 \leq \ldots \leq L_n \leq 6)$ of space $S_{\text{sym}}^n$ in turn into the right-hand side of equation (19). Some of them coincide, but the number of different ones is given by equation (18). Performing the calculations one finds 1, 3, 6 and 11 invariant directions of first, second, third and fourth order, respectively. To get the invariants of the $n$th order in strain one has to multiply $\eta_j^{L_1 \cdots L_n}$ by a general $e_{L_1} \ldots e_{L_n}$. The result is the invariant $J_j^n$ $(j = 1 \ldots j^n)$ of $n$th order corresponding to material parameter $F_j^n$ so that the $n$th degree in the free-energy expansion reads

$$F^n = \sum_{j=1}^{j^n} F_j^n J_j^n. \tag{20}$$

The invariants up to fourth order are completely listed in table 1. For later convenience, the fifth- and sixth-order invariants which are from the subspace $S_1 \oplus S_{12}$ are listed in table 2.

**Table 2.** Fifth- and sixth-order strain invariants of group $O_h$ from space $S_1 \oplus S_{12}$.

| Invariant | | Strain space |
|---|---|---|
| $J_1^5$ | $(J_1^1)^5$ | $S_1$ |
| $J_2^5$ | $(J_1^1)^3 J_2^2$ | $S_1 \oplus S_{12}$ |
| $J_3^5$ | $J_1^1 (J_2^2)^2$ | $S_1 \oplus S_{12}$ |
| $J_4^5$ | $(J_1^1)^2 J_3^3$ | $S_1 \oplus S_{12}$ |
| $J_5^5$ | $J_2^2 J_3^3$ | $S_{12}$ |
| $J_1^6$ | $(J_2^2)^3$ | $S_{12}$ |
| $J_2^6$ | $(J_3^3)^2$ | $S_{12}$ |
| $J_3^6$ | $(J_1^1)^6$ | $S_1$ |
| $J_4^6$ | $(J_1^1)^4 J_2^2$ | $S_1 \oplus S_{12}$ |
| $J_5^6$ | $(J_2^2)^2(J_2^2)^2$ | $S_1 \oplus S_{12}$ |
| $J_6^6$ | $(J_1^1)^3 J_3^3$ | $S_1 \oplus S_{12}$ |
| $J_7^6$ | $J_1^1 J_2^2 J_3^3$ | $S_1 \oplus S_{12}$ |

## 4. Adaptation of the free-energy function to copper-based alloys

Up to fourth order there are 21 material parameters necessary to determine the free-energy function. If the mentioned fifth- and sixth-order terms are included this number increases to 32. In order to handle the free-energy expansion one has to reduce this number by assumptions motivated by experimental results. The first observation is that stress-free austenite exists at high temperature. This means that for $e = 0$ the free energy must have a minimum at least at those temperatures. This is achieved by vanishing of the first-order term, i.e. $F^1 = 0$. The next observation is that at low-temperature the free energy must have 24 symmetry-related monoclinic minima. Hence there must exist a minimum in a monoclinic direction which is not invariant with respect to a subgroup of $O_h$ richer than the monoclinic group $C_2$. Translated into group-theoretical language this requirement is called the subduction and chain condition (Birman 1978). Furthermore, experiments suggest an approximation for copper-based and for some other alloys. One observes that in CuAlNi, CuZnGa, CuZn, CuAlZn, AgCd and NiAl, to each martensitic minimum of strain $e_M$ another one with nearly $-e_M$ is associated (Saburi and Wayman 1979, Okamoto *et al* 1986). We assume this relation to hold exactly. Hence one is led to the restriction

$$F(\mathbf{e}, T) = F(-\mathbf{e}, T) \tag{21}$$

which can be obeyed only if invariants of odd degree do not occur in $F$. Looking at the values of spontaneous strain of martensite in those alloys, one finds moreover that $e_1$, $e_2$ and $e_3$ are in the order of magnitude of $0.1$ whereas $e_4$, $e_5$ and $e_6$ are roughly one order of magnitude smaller. The volume change, in the linear approximation given by $3e_1^- = e_1 + e_2 + e_3$, is even smaller. Thus the main contribution to the spontaneous strain is from the irreducible space $S_{12}$ of orthorhombic symmetry, whereas the contributions from space $S_{25}$ are smaller by a factor of 10 and that from space $S_1$ is even smaller.

To obtain a first-order phase transition from an even free-energy function one has to include sixth-order terms. From the observation just described it is suggested that only sixth-order contributions from space $S_{12}$ are taken, that is the sixth-order invariants

$J_1^6 = (J_2^2)^3$ and $J_2^6 = (J_3^3)^2$ are taken into account. In fourth order we take into account every invariant of space $S_{12} \oplus S_{25}$, i.e. only volume changes (space $S_1$) are disregarded. In second order every invariant is included. This results in the free-energy function

$$F = \sum_{i=1}^{3} F_i^2 J_i^2 + \sum_{i=1}^{5} F_i^4 J_i^4 + \sum_{i=1}^{2} F_i^6 J_i^6 \qquad (22)$$

with 10 material constants $F_i^n$ which may depend on temperature. The contribution $F^0(T)$ is suppressed since it only determines the specific heat and does not influence the thermomechanical properties of the system. In order to find the minima of $F$ one has to solve the necessary condition $\partial F / \partial e_K = 0$. This equation has six types of solutions of invariant plane strain. The first type is the trivial one $e = 0$ corresponding to austenite which is stable only if the matrix $\partial^2 F / \partial e_K \partial e_L$ is positive definite at $e = 0$ or $F_1^2 > 0$, $F_2^2 > 0$ and $F_3^2 > 0$. Of the other five types only one type agrees with the subduction and chain condition. Only solutions of this type yield a monoclinic spontaneous strain which has the structure

$$
\begin{array}{llll}
e_{\bar{1}} = 0 & e_{\bar{2}} = -\alpha & e_{\bar{3}} = \alpha & e_{\bar{4}} = -\beta \\[4pt]
e_{\bar{5}} = 0 & e_{\bar{6}} = \beta & e_1 = 2\alpha & e_2 = 0 \\[4pt]
e_3 = -2\alpha & e_4 = -2\beta & e_5 = 0 & e_6 = 2\beta.
\end{array}
\qquad (23)
$$

$\alpha$ and $\beta$ are the solutions of

$$
\begin{aligned}
48\alpha^4 F_1^6 + 8\alpha^2 F_1^4 + 2\beta^2(F_4^4 + F_5^4) + F_2^2 &= 0 \\[4pt]
4\alpha^2(F_4^4 + F_5^4) + 2\beta^2(F_2^4 + 2F_3^4) + F_3^2 &= 0.
\end{aligned}
\qquad (24)
$$

Generally there are two solutions for $\alpha^2$ and $\beta^2$. Only one of them has positive values and in addition yields a minimum of the free energy. This solution is identified as one of the martensitic minima. The others follow by applying the symmetry operations of the cubic group $O_h$. Irrespective of $\alpha$ and $\beta$, i.e. of the material parameters $F_i^n$, the strain given by equation (23) always represents an invariant plane strain. The corresponding invariant plane is identified with the habit plane. Some algebra yields for their normal $n$ and for the shear vector $s$, if referred to cubic axes,

$$n = (1/k)(\alpha, \beta, \alpha) \qquad (25)$$

$$s = (1/k)[2k^2 + \alpha(\gamma - 1), \beta(\gamma - 1), -2k^2 + \alpha(\gamma - 1)] \qquad (26)$$

$$k = \sqrt{\beta^2 + 2\alpha^2} \qquad \gamma = \sqrt{1 - 8k^2} = 1 - |s|^2/2.$$

The structure of the habit-plane normal (equation (25)) is confirmed by experimental observations, for example in the alloys CuZnGa, CuAlZn, CuZn, NiAl (Saburi and Wayman 1979), AgCd (Krishnan and Brown 1973) and CuAlNi (Okamoto *et al* 1986). If the values of $\alpha$ and $\beta$ given by these authors are inserted into the shear of equation (26) then again the result describes the experimental values rather well with deviations in the shear direction of a few degrees and in the amount of 1 to 2% of the measured values.

## 5. CuAlNi alloys

In this section we determine the 10 material parameters $F_i^n$ of the free-energy function

(equation (22)) for the alloy CuAlNi by comparison with experimental results. Because of a lack of appropriate data this is not so easily done. One would like to know the elastic moduli of austenite single crystals and of martensite single variant crystals together with their temperature dependence. Unfortunately there has been, as far as we know, only a single experiment on martensitic elastic moduli of shape-memory alloys, namely on the $\gamma_1'$ martensite of Cu–14 wt%Al–3 wt%Ni by Yasunaga *et al* (1983). We thus decided to adapt the free energy to this material. However, the experiment was not done on a single variant crystal but on untwinned martensite. To recalculate the data we have to use some other theoretical idea described later. Furthermore no temperature dependence was reported. Instead we use data on the heat of transformation.

The first step is to determine $F_1^2$, $F_2^2$ and $F_3^2$ from the elastic moduli $C_{11}^A$, $C_{12}^A$ and $C_{44}^A$ of cubic austenite which are the only independent ones and are defined by

$$C_{KL}^A = \partial^2 F/\partial e_K \partial e_L \big|_{e=0}. \tag{27}$$

From equation (22) together with table 1 one finds

$$F_1^2 = \tfrac{3}{2}(C_{11}^A + 2C_{12}^A)$$
$$F_2^2 = C_{11}^A - C_{12}^A \tag{28}$$
$$F_3^2 = 2C_{44}^A.$$

The elastic moduli of a Cu–14.1 wt%Al–3 wt%Ni alloy were measured by Yasunaga *et al* (1982) and by Suezawa and Sumino (1976) for an alloy of a slightly different composition. Yasunaga *et al* report the temperature dependence of $C_{11}^A - C_{12}^A$ and of $C_{44}^A$ whereas from the data of Suezawa and Sumino the bulk modulus may be calculated: this turns out to be nearly independent of temperature. As a result we have

$$F_1^2 = 592 \text{ GN m}^{-2}$$
$$F_2^2 = (14.1 + (T - 300 \text{ K}) \times 4.6 \times 10^{-3} \text{ K}^{-1})\text{GN m}^{-2} \tag{29}$$
$$F_3^2 = (148 - (T - 300 \text{ K}) \times 9.4 \times 10^{-2} \text{ K}^{-1})\text{GN m}^{-2}.$$

One observes that austenite is highly anisotropic with a very soft shear modulus $C_{11}^A - C_{12}^A$. The seven parameters $F_i^4$ and $F_i^6$ at 300 K follow from five of the monoclinic elastic moduli of martensite together with values of the spontaneous strain measured by Okamoto *et al* (1986). From their data on habit-plane orientation $n$ and on spontaneous shear $|s|$ the values

$$\alpha = 0.023 \qquad \beta = 0.0068 \tag{30}$$

follow (equations (25) and (26)). There is some scatter in the reported value of $n$ which propagates to $\beta$. It has been mentioned that no data on the elastic moduli of internally microtwinned martensite exist. Yasunaga *et al* (1983) detwinned $\gamma_1'$ martensite prior to their experiments by applying an appropriate external stress. Their elastic moduli data referring to orthorhombic single crystals are listed in table 3. We deal here with an internally microtwinned monoclinic martensite variant which consists of layers of ortho-rhombic twins. Their amount and their orientation with respect to the austenitic parent crystal has been reported by Okamoto *et al* (1986). We assume that the elastic moduli of the microtwinned variant follow as an average over those of the single crystals. To this end the moduli of the orthorhombic twins are referred to a common system of coordinates, e.g. to the cubic axes of the parent phase. Then they are averaged according to their relative amount. The averaging has been done on the elastic moduli themselves

**Table 3.** Elastic moduli (in GPa) of orthorhombic $\gamma_1'$ martensite single crystals (untwinned) due to Yasunaga *et al* (1983) in Voigt notation.

| $C_{11}$ | $C_{22}$ | $C_{33}$ | $C_{44}$ | $C_{55}$ | $C_{66}$ | $C_{12}$ | $C_{13}$ | $C_{23}$ |
|------|------|------|------|------|------|------|------|------|
| 189 | 141 | 205 | 54.9 | 19.7 | 62.6 | 124 | 45.5 | 115 |

(as proposed by Voigt (1910)) and on their inverses which are the elastic compliances (Reuss 1929). For further calculations we use the mean values of both the results listed in table 4 if referred to base $\Phi_K$ or to the symmetry-adapted base $\Phi_{\bar{K}}$. These are compared with

$$C_{\bar{K}\bar{L}} = \partial^2 F / \partial e_{\bar{K}} \partial e_{\bar{L}} \big|_{e^M} \tag{31}$$

taken at the spontaneous strain $(e_{\bar{K}}^M) = (0, -\alpha, \alpha, -\beta, 0, \beta)$ of martensite. From equation (22) together with tables 1 and 2 one finds

$$C_{\bar{1}\bar{1}}^M = 2F_1^2 \qquad C_{\bar{1}\bar{K}} = 0 \qquad \bar{K} > 1$$

$$C_{\bar{2}\bar{2}}^M = 6F_2^2 + 120\alpha^2 F_1^4 + 12\beta^2 F_4^4 + 10\beta^2 F_5^4 + 1152\alpha^4 F_1^6 + 8\alpha^4 F_2^6$$

$$C_{\bar{3}\bar{3}}^M = 2F_2^2 + 24\alpha^2 F_1^4 + 4\beta^2 F_4^4 + 2\beta^2 F_5^4 + 192\alpha^4 F_1^6 + 8\alpha^4 F_2^6$$

$$C_{\bar{4}\bar{4}}^M = C_{66}^M = 2F_3^2 + 12\beta^2 F_2^4 + 16\beta^2 F_3^4 + 8\alpha^2 F_4^4 + 8\alpha^2 F_5^4$$

$$C_{\bar{5}\bar{5}}^M = 2F_3^2 + 8\beta^2 F_3^4 + 8\alpha^2 F_4^4$$

$$C_{\bar{2}\bar{3}}^M = -24\alpha^2 F_1^4 - 2\beta^2 F_5^4 - 288\alpha^4 F_1^6 + 8\alpha^4 F_2^6 \tag{32}$$

$$C_{\bar{2}\bar{4}}^M = 12\alpha\beta F_4^4 + 8\alpha\beta F_5^4$$

$$C_{\bar{2}\bar{6}}^M = -12\alpha\beta F_4^4 - 16\alpha\beta F_5^4$$

$$C_{\bar{3}\bar{4}}^M = -4\alpha\beta F_4^4 - 8\alpha\beta F_5^4$$

$$C_{\bar{3}\bar{6}}^M = 4\alpha\beta F_4^4 \qquad C_{\bar{4}\bar{6}}^M = -8\beta^2 F_3^4$$

$$C_{\bar{2}\bar{5}}^M = C_{\bar{3}\bar{5}}^M = C_{\bar{4}\bar{5}}^M = C_{\bar{5}\bar{6}}^M = 0.$$

**Table 4.** Elastic moduli (in GPa) of monoclinic internally twinned $\gamma_1'$ martensite (referred to symmetry-adapted base vectors). Mean value of Voigt and of Reuss averaging procedure applied to the elastic constants of the orthorhombic martensite of table 3 referred to base $\Phi_K$ and to symmetry-adapted base $\Phi_{\bar{K}}$.

| $C_{11}$ | $C_{22}$ | $C_{33}$ | $C_{44}$ | $C_{55}$ | $C_{66}$ | $C_{12}$ | $C_{13}$ | $C_{23}$ |
|------|------|------|------|------|------|------|------|------|
| 172 | 162 | 172 | 44 | 31 | 44 | 103 | 92 | 103 |

| $C_{14}$ | $C_{15}$ | $C_{16}$ | $C_{24}$ | $C_{25}$ | $C_{26}$ | $C_{34}$ | $C_{35}$ | $C_{36}$ | $C_{45}$ | $C_{46}$ | $C_{56}$ |
|------|------|------|------|------|------|------|------|------|------|------|------|
| −2.6 | 5 | 1.5 | 3.7 | −20 | −2 | −0.3 | 5 | 0.8 | 1 | −15 | −3 |

| $C_{\bar{1}\bar{1}}$ | $C_{\bar{2}\bar{2}}$ | $C_{\bar{3}\bar{3}}$ | $C_{\bar{4}\bar{4}}$ | $C_{\bar{5}\bar{5}}$ | $C_{\bar{6}\bar{6}}$ | $C_{\bar{1}\bar{2}}$ | $C_{\bar{1}\bar{3}}$ | $C_{\bar{2}\bar{3}}$ |
|------|------|------|------|------|------|------|------|------|
| 1102 | 447 | 127 | 177 | 123 | 177 | −21 | −2 | −33 |

| $C_{\bar{1}\bar{4}}$ | $C_{\bar{1}\bar{5}}$ | $C_{\bar{1}\bar{6}}$ | $C_{\bar{2}\bar{4}}$ | $C_{\bar{2}\bar{5}}$ | $C_{\bar{2}\bar{6}}$ | $C_{\bar{3}\bar{4}}$ | $C_{\bar{3}\bar{5}}$ | $C_{\bar{3}\bar{6}}$ | $C_{\bar{4}\bar{5}}$ | $C_{\bar{4}\bar{6}}$ | $C_{\bar{5}\bar{6}}$ |
|------|------|------|------|------|------|------|------|------|------|------|------|
| 1.5 | −21 | 0.3 | −3.6 | 51 | 4.8 | −12 | 50 | 7.3 | 3.9 | −61 | −12 |

**Table 5.** Elastic moduli (in GPa) of monoclinic internally twinned $\gamma_1'$ martensite (referred to base $\Phi_K$) as calculated from the free-energy function.

| $C_{11}$ | $C_{22}$ | $C_{33}$ | $C_{44}$ | $C_{55}$ | $C_{66}$ | $C_{12}$ | $C_{13}$ | $C_{23}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 181 | 170 | 181 | 44 | 31 | 44 | 112 | 101 | 112 | | | |

| $C_{14}$ | $C_{15}$ | $C_{16}$ | $C_{24}$ | $C_{25}$ | $C_{26}$ | $C_{34}$ | $C_{35}$ | $C_{36}$ | $C_{45}$ | $C_{46}$ | $C_{56}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 35 | 0 | $-26$ | $-9$ | 0 | $-9$ | $-26$ | 0 | 35 | 0 | $-15$ | 0 |

There follows the linear dependence $3C_{\bar{3}\bar{3}} - C_{\bar{2}\bar{2}} - 2C_{\bar{2}\bar{3}} = 0$, which is obeyed by the values of table 4. Together with equations (29) and (30) the five values $C_{\bar{2}\bar{2}}$, $C_{\bar{3}\bar{3}}$, $C_{\bar{4}\bar{4}}$, $C_{\bar{6}\bar{6}}$ and $C_{\bar{4}\bar{6}}$ are used to calculate the seven parameters $F_i^4$ and $F_i^6$ at 300 K:

$$F_1^4 = -1.182 \times 10^4 \text{ GN m}^{-2} \quad F_2^4 = 3.13 \times 10^5 \text{ GN m}^{-2} \quad F_3^4 = 1.64 \times 10^5 \text{ GN m}^{-2}$$

$$F_4^4 = -5.53 \times 10^4 \text{ GN m}^{-2} \quad F_5^4 = -4.27 \times 10^4 \text{ GN m}^{-2} \tag{33}$$

$$F_1^6 = 3.35 \times 10^6 \text{ GN m}^{-2} \quad F_2^6 = 3.71 \times 10^7 \text{ GN m}^{-2}.$$

In the last step their temperature dependence is investigated. The only hint is the equilibrium phase transition temperature and the heat of transformation. $T_0$ depends strongly on composition and, consequently, there is a large scatter in the values reported by different authors. We decided to use the heat of transformation reported by Otsuka *et al* (1976) to be $-48.3$ MJ m$^{-3}$ (or $-86.2$ cal mol$^{-1}$) at 300 K. Irrespective of the value chosen here the temperature dependence of $F_2^4$ and $F_3^4$ alone never sufficiently influences the value of the free energy at the martensitic minimum to produce a reasonable heat of transformation. At least one of the parameters $F_i^4$ and $F_i^6$ also has to depend on temperature. Since the major part of spontaneous strain belongs to the space $S_{12}$ we chose the only fourth-order parameter of this space, $F_1^4$, to depend linearly on the temperature:

$$F_1^4(T) = F_{10}^4 + (T - 300 \text{ K})F_{1T}^4. \tag{34}$$

The heat of transformation $Q$ follows from the entropy $S(e, T)$ defined by

$$S(e, T) = -\partial F/\partial T$$

according to

$$Q(T) = T\Delta S$$

where $T$ is the temperature of transformation and $\Delta S$ represents the difference in entropy of both the phases. For a temperature-induced transformation of a stress-free crystal one finds

$$Q(T) = T(S(e^A(T), T) - S(e^M(T), T)) = -T(4\alpha^2 F_{2T}^2 + 2\beta^2 F_{3T}^2 + 16\alpha^4 F_{1T}^4). \tag{35}$$

Together with equation (29) this yields

$$F_{1T}^4 = 35.5 \text{ GN m}^{-2}. \tag{36}$$

Equations (29), (33), (34) and (36) give the full set of parameters $F_i^n$ for the free-energy function $F(\mathbf{e}, T)$ of equation (22).

## 6. Consequences of the free-energy function

The free-energy function with the parameters just determined completely characterises the equilibrium properties of the system. In the following some of these are discussed.

At any temperature the austenitic minimum is at $e = 0$. The martensitic minima, one of them determined by equations (23) and (24), the other 23 by symmetry operations, exist below $T_c = 303$ K. Their positions in strain space, i.e. the spontaneous strain of martensite with respect to austenite, depend on temperature as shown in figure 1.
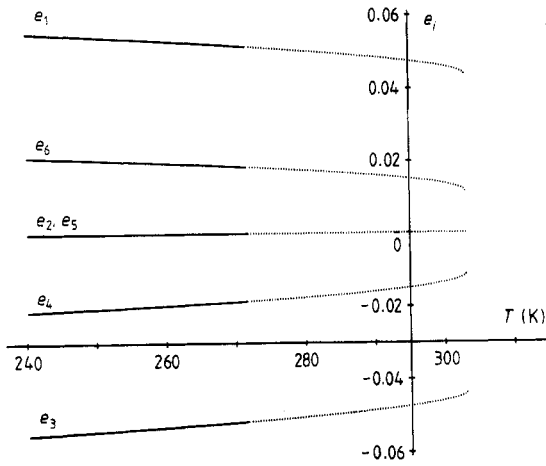


**Figure 1.** Temperature dependence of the spontaneous strain of martensite. In the dotted range martensite is metastable.

Between $T_c$ and $T_0 = 271$ K the martensitic minima have a higher free energy than the austenitic minimum. Hence in this temperature range martensite is metastable. Below $T_0$ martensite is stable, having a lower free energy than austenite. However, since the austenitic minimum does not vanish the austenite remains metastable. In figure 2 the free energy is plotted for different temperatures along a straight line in strain space joining the austenitic minimum with one of the martensitic ones. Note that the magnitude
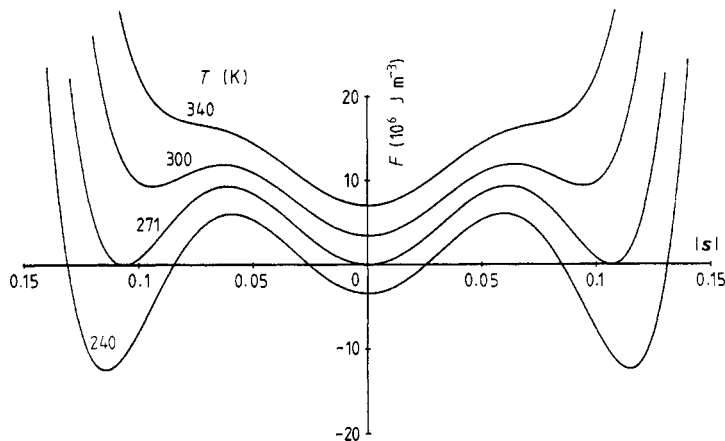


**Figure 2.** Free-energy curves for different temperatures along a straight line in strain space joining the austenitic and martensitic minima (see text for details). To avoid intersections, the different free-energy curves are shifted along the $y$ axis.

of the strain at the austenitic minima as well as the direction of the section plotted slightly depends on temperature. The lowest energy barrier does not exactly lie on the joining straight line. Instead, it is given by the energy of a saddle point which, however, is a little bit lower than the maximum energy along the straight line.

The stress–strain law derives from the free energy according to

$$\sigma_K = \partial F / \partial e_K \tag{37}$$

where $\sigma_K$ and $e_K$ refer to Voigt notation. In figure 3 the derivative of $F$ in the direction of the line joining the austenitic and martensitic minima is plotted. It describes a stress–strain curve during a shear deformation leading to one of the martensite variants. The part showing a negative slope is unstable since here an elastic modulus is negative.
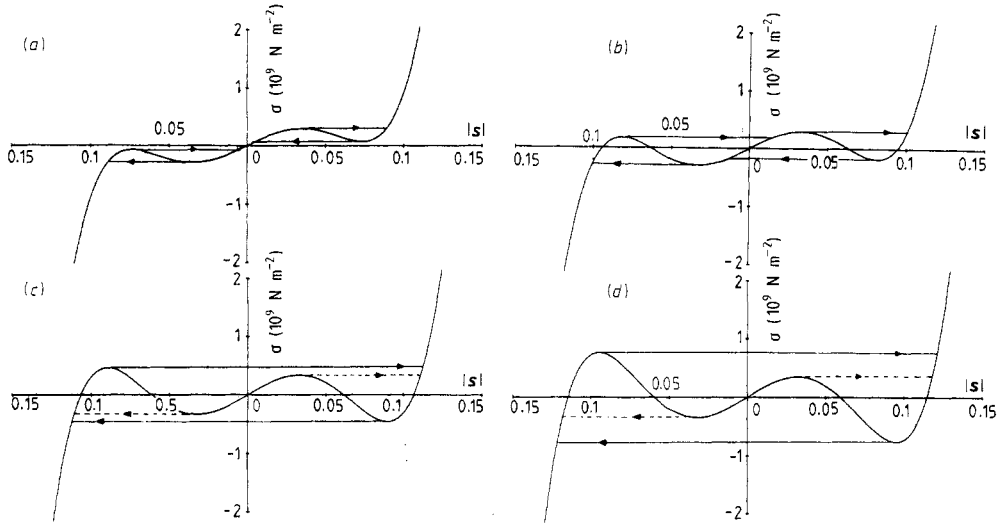


**Figure 3.** Stress–strain curve in shear along the deformation mode from austenite to martensite for different temperatures: (*a*) $T = 340$ K, (*b*) $T = 300$ K, (*c*) $T = 271$ K and (*d*) $T = 240$ K.

Therefore, with increasing stress the austenite becomes unstable when the maximum of the stress–strain curve is reached where the stress-induced transformation to martensite along the upper arrow sets in. On reducing the stress at the minimum, martensite becomes unstable and the retransformation to austenite starts. In this way the free-energy curves give rise to a stress–strain hysteresis which, however, is reduced by nucleation phenomena not included in the Landau approach. At temperatures $T > T_c$ the stress–strain curves are of pseudo-elastic type whereas at lower temperature ferro-elastic curves follow.

The elastic moduli in Voigt notation are defined by

$$C_{KL} = \partial^2 F / \partial e_K \partial e_L \tag{38}$$

where on the right-hand side the appropriate values of strain have to be inserted. In figure 4 the moduli of monoclinic martensite are plotted as functions of temperature. The values at 300 K are given in table 5. The moduli $C_{11}, C_{12}, C_{13}, C_{22}, C_{23}, C_{33}, C_{44}$, $C_{55}$ and $C_{66}$ plotted in figure 4(*a*) characterise an orthorhombic crystal whereas the rest

(figure 4(*b*)) are due to the monoclinic distortion of martensite. We would like to emphasise that the orthorhombic moduli calculated from the free energy agree rather well with experiments (compare tables 4 and 5). The monoclinic moduli are much smaller, differing from the values of table 4. This may be a consequence either of the averaging procedure necessary to get the moduli of microtwinned martensite or of neglecting third- and fifth-order terms in the free-energy expansion. This can be resolved only when experimental data on the moduli of microtwinned martensite are available. The stability or metastability range of each phase is the region in strain space in which every eigenvalue of the matrix $C_{KL}$ is positive. If one approaches the boundary of stability then the eigenvector corresponding to the vanishing eigenvalue gives the direction in strain space into which the system will evolve to a stable configuration.
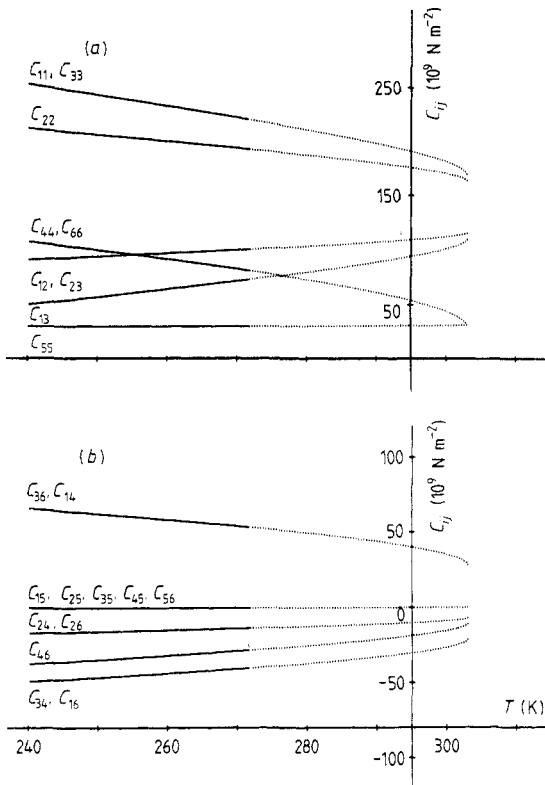


**Figure 4.** (*a*). (*b*) Elastic moduli of martensite in Voigt notation against temperature. In the dotted range martensite is metastable. The curves end where martensite becomes unstable.

In figure 5 the heat of transformation is plotted against temperature: it decreases continuously with increasing temperature. The equilibrium phase transition temperature where the free energy of both the phases coincides can be calculated numerically to yield the result

$$T_0 = 271 \text{ K.} \tag{39}$$

Salzbrenner and Cohen (1979) suggest that $T_0$ is identified with $(M_s + A_f)/2$. Calculated values over a wide range are reported by different authors (see e.g., Otsuka *et al* 1976, Okamoto *et al* 1986, Yasunaga *et al* 1982).
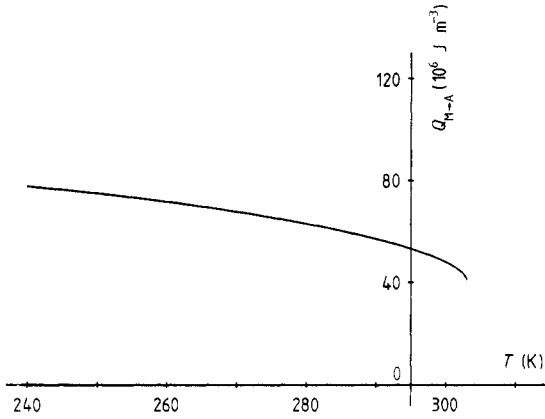
Figure 5. Heat of transformation of stress-free crystals against temperature.

## 7. Discussion

As it stands the free energy proposed in the present paper describes homogeneous shape-memory alloys, i.e. one-phase single crystals in which the strain does not vary. In order to deal with more involved cases, for example with strain depending on position or even with multiphase crystals, one has to embed the free energy as a constitutive equation into the basic laws of continuum mechanics, namely into the balance of mass, of momentum and of energy. Restrict oneself to isothermal equilibrium, then only the balance of momentum is relevant which then reads

$$\nabla \cdot \boldsymbol{\sigma} + f = 0 \tag{40}$$

within the body and

$$\boldsymbol{n} \cdot \boldsymbol{\sigma} = a \tag{41}$$

at the surface, where $f$ and $a$ denote external volume and surface force densities, respectively, and $\boldsymbol{n}$ is the outer normal of the surface of the body. Typically, $f$ is due to gravity and may be neglected. Since the free energy contains terms higher than second order the stress is a non-linear function of strain, which results in the non-linear balance equations (40) and (41). It is thus rather cumbersome to solve these equations for arbitrary surface forces or in the case of defects such as dislocations. In some special cases, however, the problem reduces to one dimension. Assume for example a parallelepiped with edges parallel to the habit plane, the orientation of which follows from the free energy according to equations (25) and (24). Furthermore, consider constant external forces acting on the surface parallel to the habit plane only. Then the solution of the balance equations is a shear deformation parallel to the habit plane varying only in a direction normal to it. The shear is proportional to that given by equation (23). If one denotes its amount by $s$ the free energy for this special deformation mode is given by

$$F(s, T) = a_6 s^6 - a_4 s^4 + a_2 s^2 \tag{42}$$

with temperature-dependent positive coefficients $a_i$ following from the parameters $F_i''$. Together with the stress–strain curves in shear the result is plotted in figures 2 and 3. This free-energy function is exactly of the type proposed by Falk (1980) in a purely one-dimensional approach. A two-phase system consisting of layers of austenite and

martensite is represented by a one-dimensional deformation of the type just discussed in which the strain jumps from the value of austenite to that of martensite across the habit plane. The dynamics of this problem was treated by Falk and Seibel (1987).

Since the free energy proposed in the present paper yields 24 martensitic variants one can deal with self-accommodating groups of four variants in an austenitic matrix. For example, four variants with

$$(e_K)_I = (0, -2\alpha, 2\alpha, 0, -2\beta, -2\beta)$$

$$(e_K)_{II} = (0, 2\alpha, -2\alpha, 0, 2\beta, 2\beta)$$

$$(e_K)_{III} = (0, 2\alpha, -2\alpha, -2\alpha, 0, -2\beta, -2\beta)$$

$$(e_K)_{IV} = (0, -2\alpha, 2\alpha, 0, 2\beta, 2\beta)$$

yield a vanishing mean value of strain. They have habit planes with normals

$$n_I = (\beta, \alpha, -\alpha) \qquad n_{II} = (\beta, \alpha, -\alpha)$$

$$n_{III} = (-\beta, \alpha, -\alpha) \qquad n_{IV} = (-\beta, \alpha, -\alpha).$$

Moreover, the relative strain from one variant to another is an invariant plane strain for the pairs I–III, I–IV, II–III and II–IV with normals $(0,1,-1)$, $(1,0,0)$, $(1,0,0)$ and $(0,1,-1)$, respectively. Therefore in this group every interface is stress-free.

In further investigations heterogeneous nucleation can be treated. Up to now there have been attempts in this direction by Clapp (1973), Guénin and Clapp (1986) and Olson and Cohen (1982). In these papers, however, an inappropriate one-dimensional free energy is used. Taking the three-dimensional free energy proposed for the first time in this paper, one has to solve the balance equation (40) for defects such as dislocations of different types and different orientations. Because of the highly non-linear stress–strain relation this can be done only numerically. It is expected that at least for a metastable phase around a dislocation core an embryo of the new phase exists in equilibrium.

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