One-dimensional model of shape memory alloys

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THE AIM of this paper is to present a one-dimensional model of shape memory alloys. The purpose of this model is not so much to give quantitative results but to reflect the qualitative behaviour of those alloys. Within the framework of Landau theory we restrict ourselves to single crystals, which have a slowly varying shear strain ε. We look for a Helmholtz free energy density F as a function of the strain ε and of the temperature T which gives us the equations of state. Further, in the Ginzburg–Landau theory, we add a term depending on the gradient of the strain which accounts for the presence of phase boundaries and measures the lattice curvature. The most simple possibility is chosen and the gradient of strain squared with a constant coefficient δ is added.

Celem pracy jest przedstawienie jednowymiarowego modelu stopów z pamięcią kształtu pozwalającego uzyskać nie tyle ilościowe, ile raczej jakościowe właściwości tego rodzaju stopów. W ramach teorii Landaua ograniczamy się do monokryształów z powolnie zmieniającym się odkształceniem ścinającym ε. Wyrażenia na gęstość energii swobodnej Helmholtza poszukujemy w postaci funkcji odkształcenia ε i temperatury T, co prowadzi do uzyskania równania stanu. Następnie, zgodnie z teorią Ginzburga–Landaua, uzupełniamy równanie członem zależnym od gradientu odkształcenia uwzględniającym wpływ obecności granic międzyfazowych i określającym krzywiznę sieci. Wybrano najprostszą możliwość dodając człon zawierający kwadrat gradientu odkształcenia ze stałym współczynnikiem δ.

Целью работы является представление одномерной модели сплавов с памятью формы, позволяющей получить не столько количественные, но скорее качественные свойства этого типа сплавов. В рамках теории Ландау ограничиваемся монокристаллами с медленно изменяющейся деформацией сдвига ε. Выражения для плотности свободной энергии Гельмгольца ищем в виде функции деформации ε и температуры T, что приводит к получению уравнения состояния. Затем, согласно теории Гинзбурга-Ландау, пополняем уравнение членом, зависящим от градиента деформации, учитывающим влияние присутствия межфазных границ и определяющим кривизну решетки. Избрана самая простая возможность, добавляя член, содержавший квадрат градиента деформации с постоянным коэффициентом δ.

1. Introduction

THE AIM of this paper is to present a one-dimensional model of shape memory alloys. The purpose of this model is not so much to give quantitative results but to reflect the qualitative behaviour of these alloys.

It is well known that the shape memory effect is due to a first-order martensitic phase transition. This phase transition is responsible not only for the shape memory effect in these alloys but also for their pseudoelastic and ferroelastic behaviour (see for example the review papers [1, 2, 3, 4]). In Fig. 1 the typical stress-strain curves are plotted for different temperatures. At high temperature the alloys show linear elastic behaviour. At intermediate temperature we get a pseudoelastic (superelastic) stress-strain relation whereas at low temperature the material behaves ferroelastically.
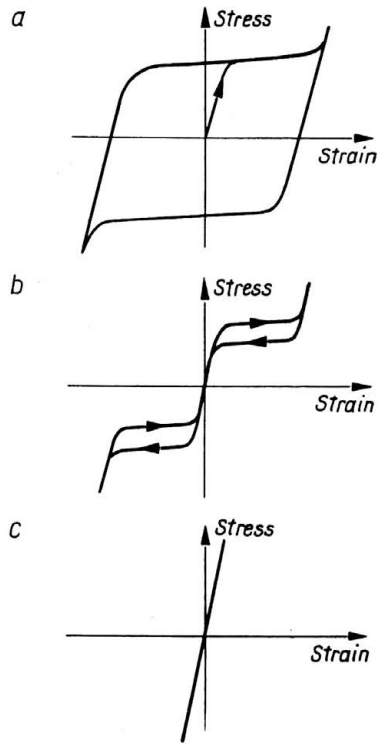
FIG. 1. Typical stress-strain curves of shape memory alloys at different temperatures. a) Low temperature, ferroelastic behaviour. b) Intermediate temperature, pseudoelastic behaviour. c) High temperature, linear elastic behaviour.
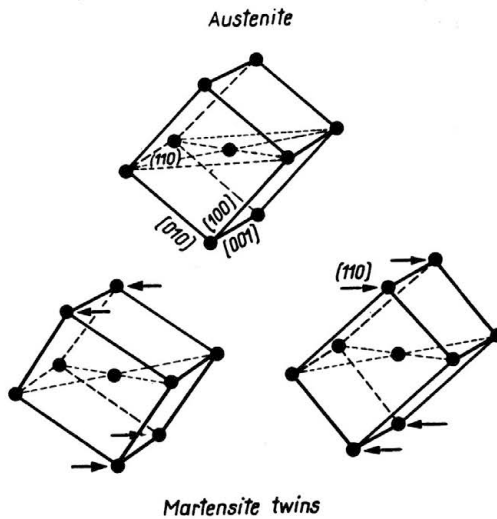

Austenite

Martensite twins

FIG 2. Crystal structure of austenite and martensite.

In order to develop the model, we look at the crystal structure of these alloys (Fig. 2). At high temperature most of them, as for example NiTi, CuZn, CuSn, $AuCuZn_2$, AuCd, AgCd, have an ordered bcc structure. This high-temperature phase is called austenite (or β-phase). On cooling the first-order martensitic phase transition takes place transforming the crystal to martensite. This transformation is nearly volume preserving. The change in volume typically is less than 0.5%. Essentially the transformation is a shear on a plane near to $\{110\}$ with the direction of shear $\langle 1\overline{1}0 \rangle$. The order of magnitude of the shear is 10%. Since there is more than one such plane and direction, we can get 24 variants of martensite from one given austenite crystal.

2. One-dimensional model

In the one-dimensional model we restrict ourselves to an applied shear stress on one (110)-plane in one [$1\overline{1}0$]-direction, positive or negative. Therefore we can get only two martensite variants which are twins.

In the model we construct the crystal by stacking layers which are parallel to the shear plane (Fig. 3). Each layer is homogeneous and may deform by shearing to the right or to the left. The amount of shear is denoted by ε. Undeformed austenite corresponds to vanishing ε. This reference state is used throughout this paper even at temperatures where austenite is unstable.
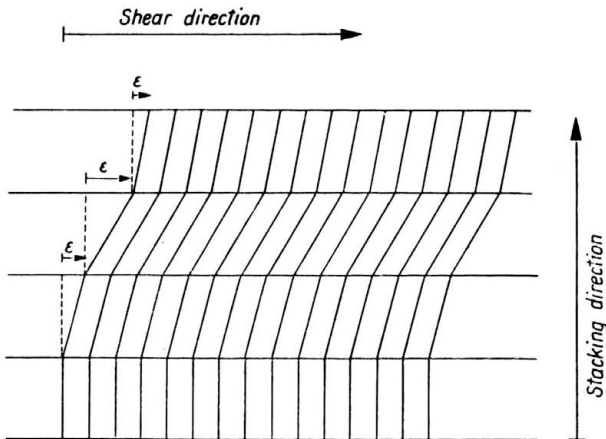

FIG. 3. One-dimensional model. The crystal is built up by stacking of crystal layers parallel to the (110)--plane. Stacking direction [110], shear direction [$1\overline{1}0$].

3. Landau theory

3.1. Free energy

Within the framework of the Landau theory [5, 6], we restrict ourselves to single crystals which have a slowly varying shear strain ε. In order to apply the theory of thermoelasticity, we have to look for a Helmholtz free energy density F as a function of the strain ε and of the temperature T which gives us the equations of state.

This function has to meet the following requirements:

1) F is symmetric with respect to ε since shearing to the right and to the left are equivalent.

2) At high temperatures only undeformed austenite is stable. Therefore F must have only one minimum at vanishing ε.

3) At low temperatures only martensite is stable. F must have two symmetric minima corresponding to the martensite twins.

4) At intermediate temperatures austenite and martensite are stable or metastable. F has three minima.

5) F should go to infinity for big ε.

The simplest function satisfying these conditions is

$$(3.1) \qquad F(\varepsilon, T) = \alpha\varepsilon^6 - \beta\varepsilon^4 + \gamma(T - T_1)\varepsilon^2 + F_0(T), \qquad \alpha, \beta, \gamma, T_1 > 0, \text{const.}$$

$F_0(T)$ is some smooth function of temperature which for most purposes does not matter.

In the following we shall discuss the mechanical and thermodynamic consequences of this one-dimensional Landau free energy function. We find that Eq. (3.1) gives us qualitatively the whole variety of observed behaviour of shape memory alloys. Furthermore it is possible to derive a free energy function from statistical mechanics, which is of the same type [7, 8].

In order to simplify the discussion, it is convenient to introduce dimensionless quantities which in the following are denoted by lower case letters

$$(3.2) \qquad f = \frac{\alpha^2}{\beta^3} F, \quad e = \sqrt{\frac{\alpha}{\beta}}\, \varepsilon, \quad t = \frac{\alpha\gamma}{\beta^2}(T - T_1) - \frac{1}{4}.$$

We get

$$(3.3) \qquad f = e^6 - e^4 + \left(t + \frac{1}{4}\right) e^2 + f_0(t).$$

The Landau model contains 4 parameters $\alpha, \beta, \gamma, T_1$ which have to be chosen according to the specific material (see Chapter 3.10). In rescaled units the free energy is independent of any parameter. This means that we have a theorem of corresponding states as known from a van der Waals gas.

In Fig. 4 the Helmholtz free energy is plotted as a function of shear strain e for different temperatures. The 5 requirements we posed on f are complied with.

For $t > 1/12$ the free energy has one minimum at $e = 0$ only. Only austenite is stable in this range of temperature.

For $-1/4 < t < 1/12$ there are three minima.

If $t > 0$, the austenitic minimum at $e = 0$ is the lowest one. Therefore austenite is stable and the martensite twins are metastable.

If $t = 0$, all three minima are of equal depth.

For $-1/4 < t < 0$ the martensitic minima are lower than the austenitic one and therefore austenite is metastable and martensite is stable.

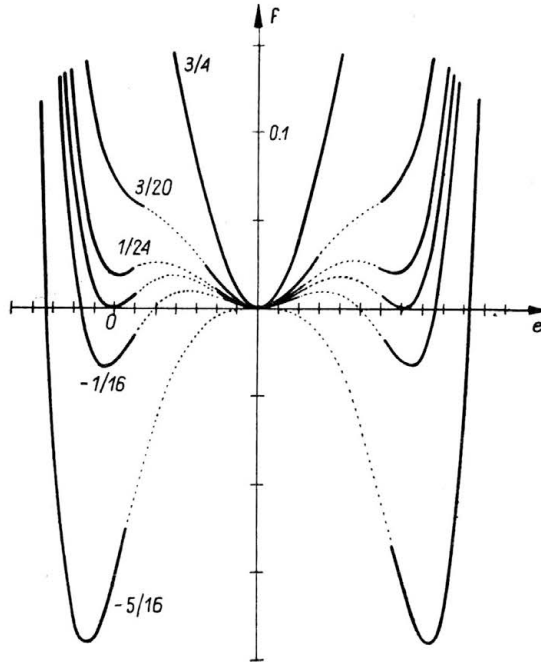For $t < -1/4$ there is no austenitic minimum. Only martensite is stable.

FIG. 4. Helmholtz free energy f over shear strain e with temperature t as parameter (Eq. (3.3), $f_0(t)$ omitted). In the dotted region the crystal is unstable.

The martensitic minima are located at the strain

$$(3.4) \qquad e_0 = \pm \sqrt{\frac{1}{3} + \frac{1}{6}\sqrt{1-12t}}\,, \quad t < 1/12.$$

Note that one free energy function applies to three different phases. The dotted parts of the curves correspond to unstable regions which will become apparent in the next chapter. Since Helmholtz free energy is a thermodynamic potential as a function of strain and temperature, all thermodynamical functions can be derived. We shall do this in the following.

3.2. Stress-strain relation

By definition the shear stress σ is the response of the system on deformation.

$$(3.5) \qquad \sigma = \frac{\partial f}{\partial e} = 6e^5 - 4e^3 + 2\left(t + \frac{1}{4}\right)e.$$

The stress strain-curves are antisymmetric with respect to strain (Fig. 5). At high temperature the stress-strain curve is nearly linear. The crystal is linear elastic. For lower temperature we have a nonlinear behaviour. In the range $7/20 > t > 1/12$ we have pseudoelasticity. On loading austenite deforms continuously until the maximum of the curve is reached. In the dotted region the shear stress would diminish on further deformation. This part of the curves is an unstable region. In reality the crystal undergoes a phase transition from austenite to martensite along the upper arrow. This means that on load-

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ing more and more austenite transforms to martensite until no austenite is left. Along the arrow we have a mixture of two phases. Further loading leads to a deformation of martensite. If we reduce the load, the deformation of martensite goes back until the minimum of the curve is reached. The retransformation from martensite to austenite takes place along the lower arrow. In the pseudoelastic temperature domain we have a hysteresis in the stress-strain curves. On cooling, the hysteresis grows until at $t = 1/12$; it is so big that its lower boundary arrives at vanishing stress. This means that for $t < 1/12$ unload-
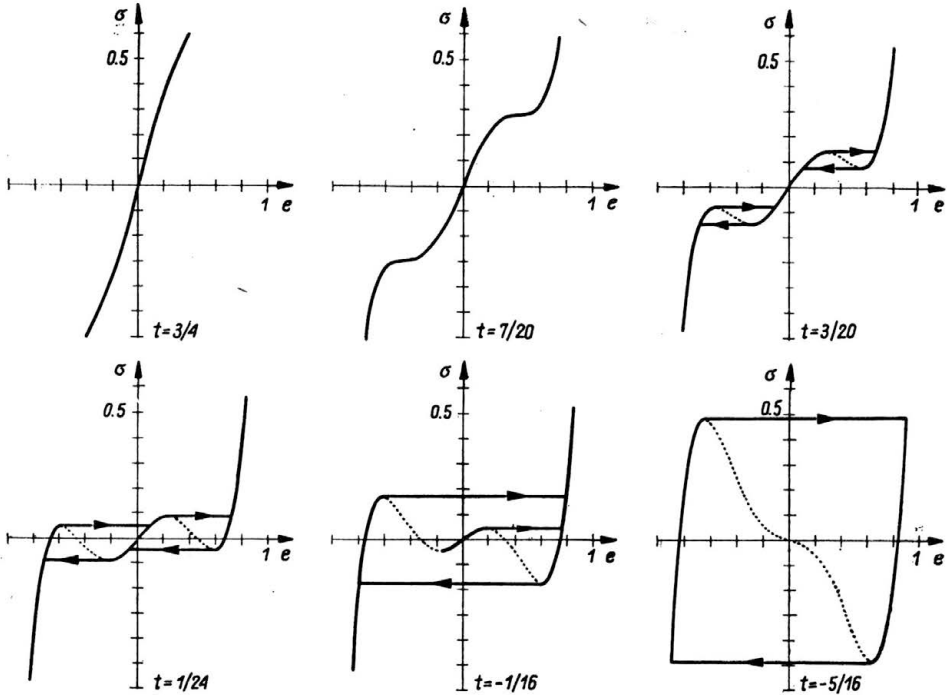

FIG. 5. Shear stress σ over shear strain e for different temperatures t (Eq. (3.5)). Unstable regions are dotted.

ing of martensite results in stress-free martensite with strain e_0 (Eq. (3.4)). For these temperatures the crystal is ferroelastic. The reverse transformation to austenite occurs only on loading in the opposite direction. If $1/12 > t > 1/60$, the reverse transformation goes from the right martensite twin M^+ to austenite and only on further reverse loading to the left martensite twin. If $t < 1/60$, the reverse loading leads to a phase transition from the right martensite twin directly to the left one. If $t < -1/4$, the austenitic part of the stress-strain curves disappears and we have a ferroelastic behaviour of the martensite twins.

Notice that the stress-strain relation is not one-to-one. To each stress there correspond up to three values of strain. In order to make this relation unique we have to know which phase of the system is considered. In this way we get a first-order stress induced phase transition with hysteresis, if temperature is lower than $t_{cr} = 7/20$. On the isotherm t_{cr} we have a critical point at $e_{cr} = 1/\sqrt{5}$, $\sigma_{cr} = 16/(25\sqrt{5})$.

Up to now we were engaged with the highest possible hysteresis which was determined by the dotted region of instability. If we are interested in the equilibrium phase transition, we have to look more closely at our curves. If there is an unstable region with a negative slope in the stress-strain relation, we have a concave part in the free energy (Fig. 6). Therefore there is a common tangent at two points of the free energy curve which gives us a lower free energy than the curve itself. This tangent represents the mixture of austenite of strain e_A and martensite of strain e_M. Since in equilibrium free energy is mini-
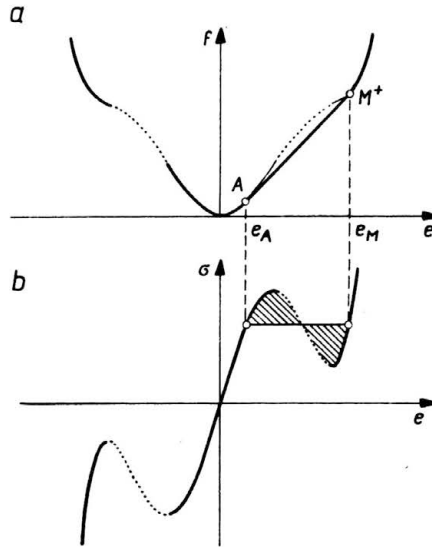

FIG. 6. Maxwell's rule of equilibrium phase transition in the f-e-plot (a) and in the σ-e-plot (b).
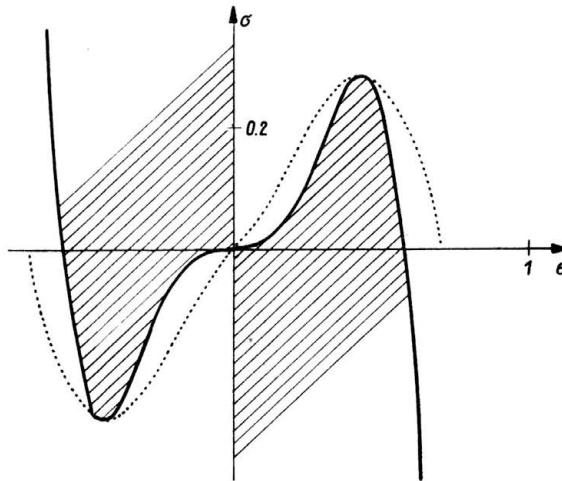

FIG. 7. Spinodal (solid curve) and line of equilibrium phase transition (dotted curve) in stress-strain space. The shaded area bound by the spinodal is an unstable region. The domain between both curves is the region of superstraining.

mal, the equilibrium phase transition goes along this tangent. When we arrive at point A phase separation begins. On loading more and more austenite transforms to martensite until the whole crystal has transformed at point M^+. Translating this construction to the stress-strain curve we get Maxwell's line which equates the shaded areas. The construction is well known in the liquid-vapour phase transition of a van der Waals gas.

Now we can construct in stress-strain space the region of instability (Fig. 7). In the language of phase transition the curve binding the unstable region is called spinodal. In the region inside the spinodal a stable one-phase configuration does not exist. In the same diagram we can draw the curve where the equilibrium phase transition takes place. This curve bounds the region where in equilibrium austenite and martensite coexist. The region between the curves is the domain of superstraining.

3.3. Elastic constant

The next point is to calculate the elastic shear "constant", which is defined as derivative of the stress with respect to the strain and therefore depends on strain and temperature.

$$c = \frac{\partial \sigma}{\partial e} = \frac{\partial^2 f}{\partial e^2} = 30e^4 - 12e^2 + 2\left(t + \frac{1}{4}\right).$$

In our model the shear is on an (110)-plane in the $[1\bar{1}0]$-direction. Therefore the elastic constant corresponds to $C' = \frac{1}{2}(C_{11} - C_{12})$.

From the definition we get the elastic constant as a function of strain and temperature. Of particular interest are the values for austenite and martensite at vanishing stress. For austenite this is equivalent with vanishing strain. In the case of martensite we have to insert the value $e_0(t)$ denoting the strain of stress-free martensite (Eq. (3.4)).

(3.6)
$$c_A(t) = 2t + 1/2,$$
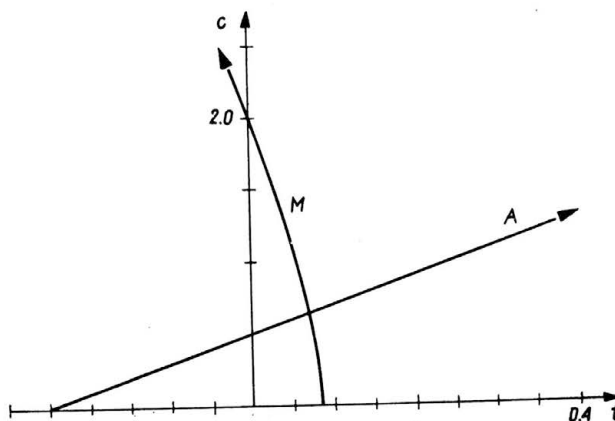$$c_M(t) = 2/3(1 - 12t) + 4/3\sqrt{1 - 12t}.$$

FIG. 8. Elastic shear constant c of stress-free austenite (A) and martensite (M) as a function of temperature t (Eq. (3.6)).

The result is remarkable (Fig. 8). On heating we have a rapid decrease of the elastic constant of martensite until it vanishes at $t = 1/12$ where martensite becomes unstable.

The elastic constant of austenite, however, decreases on cooling linearly, vanishing at the stability boundary of austenite at $t = -1/4$. This behaviour is irregular. Experiments, however, show this lattice softening. One says that the phase transition is induced by an elastic instability. ZENER was the first to notice this fact for bcc metals in 1947 [9].

3.4. Entropy, internal energy, Gibbs free energy

The entropy is defined by $s = -\partial f/\partial t$ and we get

$$(3.7) \qquad s = -e^2 - df_0(t)/dt.$$

We notice that the entropy is added up by a strain dependent and a temperature-dependent part. From entropy and Helmholtz free energy we can calculate the internal energy

$$(3.8) \qquad u = f + (t+t_0)s, \qquad t_0 = \frac{1}{4} + \frac{\alpha\gamma}{\beta^2} T_1,$$

$$u = e^6 - e^4 + \left(\frac{1}{4} - t_0\right)e^2 + f_0(t) - (t+t_0)\frac{df_0}{dt}.$$

The term t_0 appears because the rescaled temperature t is shifted against the absolute temperature T (Eq. (3.2)).

We find that the internal energy splits in two independent parts too. Therefore the u over e curves for different temperatures are simply displaced parallel without changing shape.

If we look at the definition of the internal energy (Eq. (3.8)), we notice that the great variety of f over e curves results from the term ts. Therefore the characteristic stress-strain relations of shape memory alloys are due to entropy. Thus these alloys are called entropy elastic or rubber elastic since in rubber elasticity is due to entropy, too.

Gibbs free energy is defined by

$$(3.9) \qquad g(\sigma, t) = f(e(\sigma, t), t) - \sigma e(\sigma, t).$$

Gibbs free energy is a thermodynamic potential only as a function of stress and temperature, and we have to replace the strain by the stress. This, however, can be done only numerically (Fig. 9). We have to bear in mind that the stress-strain relation is not one-to-one. For each of the phases austenite, right, and left martensite twin, we have a separate stress-strain relation. Therefore we get three different curves for Gibbs free energy, one for each phase. Each curve ends at the point where the corresponding phase loses stability. In equilibrium the system exists in the phase with the lowest Gibbs free energy. The equilibrium phase transition takes place at the intersection of the Gibbs free energy curves. The part between the intersections and the ends of the curves correspond to superstraining.

Because of the nonuniqueness of Gibbs free energy, Helmholtz free energy which is unique seems more convenient for describing shape memory alloys.
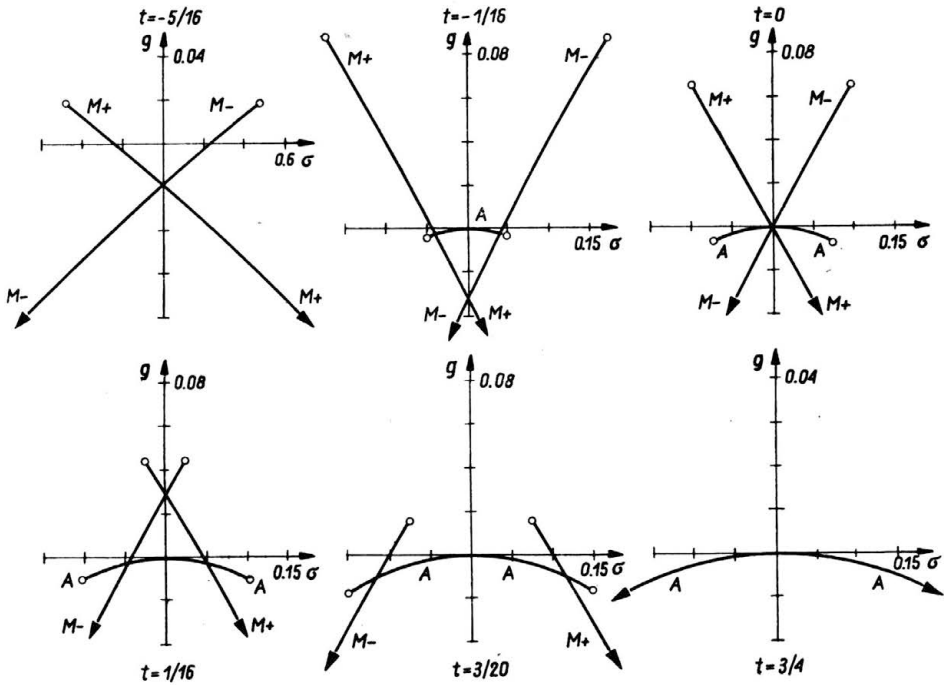
FIG. 9. Gibbs free energy g over stress σ for different temperatures t. The curves marked by A, M^+, and M^- apply to austenite, right, and left martensite twin, respectively. The curves end at the dots where the corresponding phases become unstable.

3.5. Specific heat

The specific heat is defined by the heat supply over the change of temperature

$$(3.10) \qquad C = \frac{\delta Q}{\delta T} = T \frac{\partial S}{\partial T}.$$

We have to distinguish whether stress or strain is fixed.

In the case where strain is fixed we simply get

$$(3.11) \qquad c_e(t) = (t+t_0) \frac{\partial s(e, t)}{\partial t} = -(t+t_0) \frac{d^2 f_0}{dt^2},$$

which is a continuous function of temperature alone. c_e is independent of strain and therefore the same function for austenite and martensite.

If we fix the stress, we have

$$(3.12) \qquad c_\sigma(\sigma, t) = (t+t_0) \frac{\partial s(\sigma, t)}{\partial t} = (t+t_0) \left(\frac{\partial s(e, t)}{\partial t} + \frac{\partial s(e, t)}{\partial e} \frac{\partial e(\sigma, t)}{\partial t} \right)$$

$$= c_e(t) - 2e(\sigma, t)(t+t_0) \frac{\partial e(\sigma, t)}{\partial t},$$

c_σ is different for austenite and martensite even at the same stress and temperature since the strain as a function of stress differs for both phases. In the stress-free case we get for austenite with vanishing strain at vanishing stress

$$c_{\sigma_A}(\sigma = 0, t) = c_e(t).$$

For martensite at $\sigma = 0$ we have $e = e_0(t)$ (Eq. (3.4)) getting (Fig. 10)

$$(3.13) \qquad c_{\sigma_M}(\sigma = 0, t) = c_e(t) + \frac{t + t_0}{\sqrt{1 - 12t}}.$$

The difference between the specific heat at vanishing stress of austenite and martensite has an integrable singularity at the temperature where martensite becomes unstable.
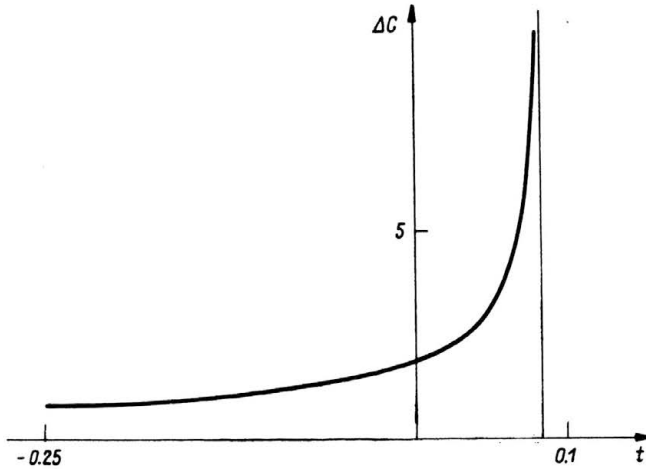

FIG. 10. The difference Δc between specific heat of martensite with stress or strain fixed (Eq. (3.13)) plotted over temperature t. There is an integrable singularity at $t = 1/12$ where martensite becomes unstable. t_0 is taken from Eq. (3.8) with α, β, and γ according to Chapter 3.10 ($t_0 = 1.91$).

3.6. Temperature-induced phase transition

The martensitic phase transition can be induced not only by loading at fixed temperature but also by heating or cooling at fixed load.

Figure 11 shows the strain-temperature curves at constant load. For large load instability does not occur nor does a phase transition. For $\sigma < 16/(25\sqrt{5}) = \sigma_{cr}$, cooling of austenite leads to a phase transition at that temperature where the boundary of stability is reached, namely at the broken curve. The crystal transforms to martensite M^+ which, on further cooling, does not deform very much. On heating the boundary of instability for martensite is reached at higher temperatures only. Then the reverse transformation to austenite occurs. Therefore we get thermal hysteresis. The broken curve bounds the unstable region and is called spinodal.

The dash-dotted curve connects the points where the equilibrium phase transition takes place. Therefore the region between the broken and the dash-dotted curves indicates the possible superheating or supercooling.

In practice it is not obvious to what extent supercooling or superheating takes place. We can only argue that in an elastically homogeneous, unstressed single crystal the temperature at which, on cooling, the formation of martensite starts has to be in the domain $[-1/4,0]$. Analogously the temperature where, on heating, the formation of austenite starts has to be in the domain $[0,1/12]$.
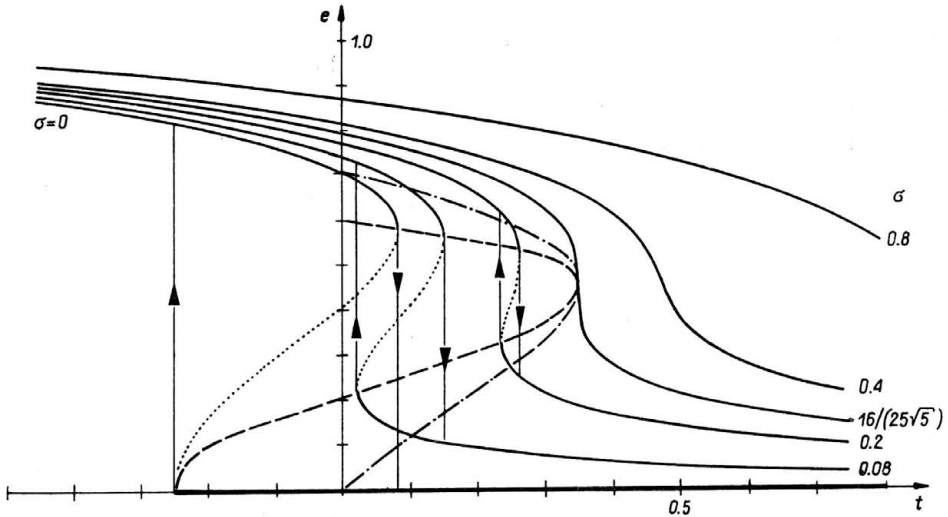

FIG. 11. Strain e over temperature t for different stresses σ. The dotted regions correspond to unstable states which are bounded by the dashed curve. The arrows indicate the temperature-induced phase transition in the case of highest possible hysteresis. At the dash-dotted curve the equilibrium phase transition takes place.

If there are lattice defects, the crystal is self-stressed. Thus we have a distribution of shear stress which in the neighbourhood of the defects varies rapidly. Since the temperature of the equilibrium phase transition as well as the boundaries of the stable domains depend on the stress, these temperatures will vary within the crystal, too. Consequently, on cooling the austenite-to-martensite phase transition begins earlier in regions where by self-stress the temperature of the phase transition is raised. In this way defects serve as nuclei for the new phase.

In this model it is possible to have a continuous transition from austenite to martensite if we heat austenite to $t > t_{cr}$, then apply a load $\sigma > \sigma_{cr}$ and cool down below t_{cr}, that is if we go round the critical point. This is in analogy to the liquid-vapour phase transition.

The driving force for the phase transition at fixed stress is the difference between the Gibbs free energies of both phases. In the case of vanishing stress the driving force is plotted as a function of temperature in Fig. 12. At $t = 0$ the driving force vanishes. This means that at this temperature the phases are in equilibrium. At lower temperature the driving force from austenite to martensite is positive. The curve ends at that temperature at which austenite or martensite becomes unstable. The driving force varies nearly linearly with supercooling.
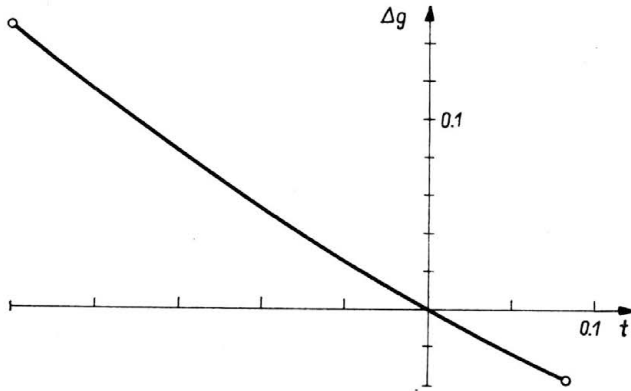
FIG. 12. Driving force for the phase transition from austenite to martensite over temperature at vanishing stress. The curve ends at $t = -0.25$ and $t = 1/12$ since beyond these temperatures only one of the phases is stable.

3.7. Latent heat

The latent heat of the phase transition from austenite to martensite is defined by

(3.14) $$q = (t+t_0)\Delta s = (t+t_0)\big(s(e_A, t) - s(e_M, t)\big),$$

e_A and e_M are the strain of austenite and martensite, respectively. We get

(3.15) $$q = (t+t_0)(e_M^2 - e_A^2).$$

For vanishing load we have $e_A = 0$ and $e_M = e_0(t)$ (Eq. 3.4) and, consequently, (Fig. 13)

(3.16) $$q(\sigma = 0, t) = (t+t_0)\left(\frac{1}{3} + \frac{1}{6}\sqrt{1-12t}\right).$$

In the domain $-1/4 < t < 1/12$, where both phases can coexist, the latent heat does not depend very much on temperature, that is on supercooling or superheating. Its lowest possible value lies at that temperature where martensite becomes unstable.
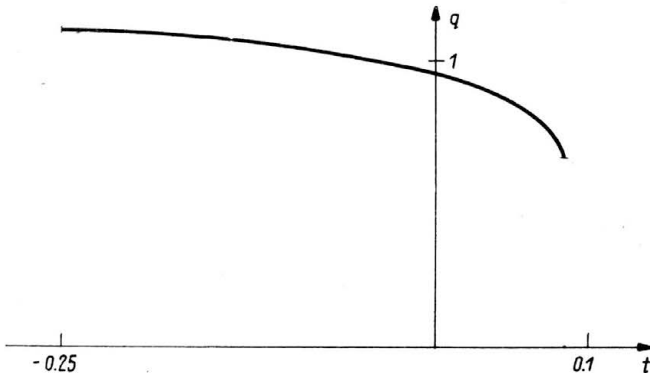

FIG. 13. Latent heat of the phase transition from martensite to austenite if stress vanishes (Eq. (3.16)). The curve ends at $t = -0.25$ and $t = 1/12$.

3.8. Phase diagram

With the calculated data we can plot a phase diagram in stress-temperature space (Fig. 14).
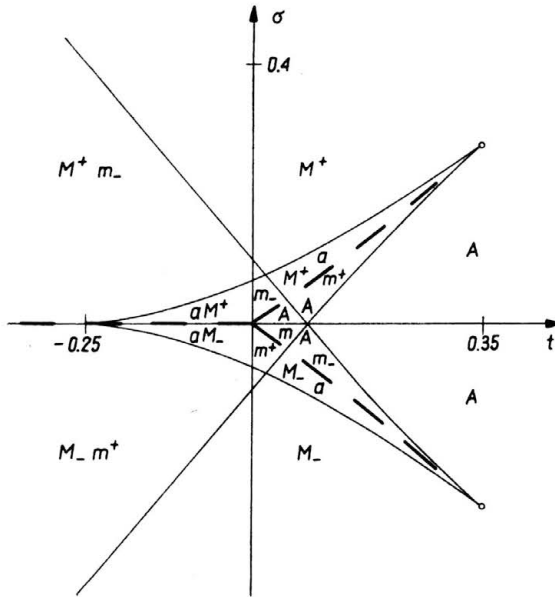

FIG. 14. Phase diagram in stress-temperature space. Capital letters (A, M^+, M_-) denote stable phases, small letters (a, m^+, m_-, m) metastable phases. $A(a)$, $M^+(m^+)$, $M_-(m_-)$, and m correspond to austenite, right martensite twin, left martensite twin, and either martensite twin, respectively. The solid lines separate the region where a phase is metastable from the region where the same phase is unstable. The bold broken line separates regions of metastability from regions of absolute stability. At $t = 0$, $\sigma = 0$ three phases are stable. In the neighbourhood of this point, three phases, one stable and two metastable, may coexist.

3.9. Shape memory effect

The shape memory effect is characterized by the fact that a permanent strain created by loading at low temperature vanishes on heating. This effect is accounted for in our model (Fig. 15).
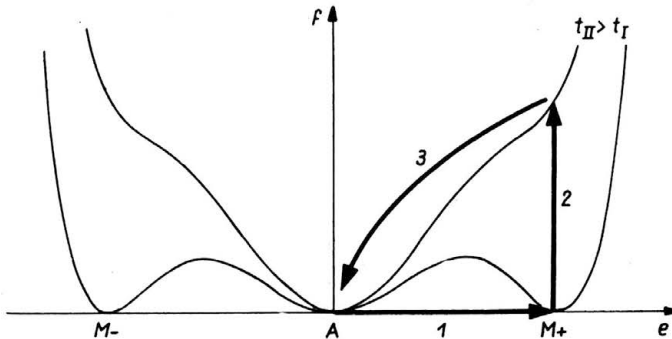

FIG. 15. Shape memory effect in an f-e-plot (see text).

We start at low-temperature t_I with undeformed austenite. If in a first step we apply a big enough load, the crystal transforms to martensite M^+. Since the free energy curve has a martensitic minimum, the crystal remains in this phase even when we remove the load. We have generated a permanent strain. Now if we, in a second step, heat the crystal to the temperature t_{II}, we shift to a free energy curve which has no martensitic minimum at all. The crystal spontaneously retransforms to undeformed austenite and retains its original shape. If we cool to the starting temperature t_I, nothing more happens. To get this behaviour we have to start with a temperature in the range $-1/4 < t_I < 1/12$ and heating must exceed $t = 1/12$.

3.10. Determination of parameters

The Landau-model can be fitted to a specific material only by the four parameters $\alpha, \beta, \gamma, T_1$. The model is adapted to single crystals and experiments for the comparison should have been done on single crystals, too.

Measurements concerning hysteresis phenomena are not suitable because we can calculate the highest possible hysteresis for crystals without defects only, which may not be reached. Since the properties of shape memory alloys strongly depend on chemical composition, so do the parameters. Therefore one has to be careful in using data from different authors.

For the alloy $Au_{23}Cu_{30}Zn_{47}$ Y. MURAKAMI [10] published a sufficient set of data, namely latent heat, equilibrium phase transition temperature T_0 at vanishing stress and the elastic shear constant of austenite at different temperatures. The latter shows a linear decrease on cooling which is in agreement with the model.

The slope of the elastic constant gives us the parameter γ. By extrapolating the elastic constant to zero, we find the stability boundary of austenite at zero stress which is T_1. From the latent heat and the equilibrium phase transition temperature we get β and α:

$$\alpha = 7.5 \cdot 10^6 \text{ Jcm}^{-3}, \qquad \gamma = 24 \text{ Jcm}^{-3}\text{K}^{-1},$$
$$\beta = 1.5 \cdot 10^5 \text{ Jcm}^{-3}, \qquad T_1 = 208 \text{ K}.$$

From these values we can calculate the strain of unstressed martensite at the equilibrium phase transition temperature to 0.10 corresponding to the shear angle 5.7°. Unfortunately Murakami did not mention an experimental value. However, a shear of this magnitude typically occurs in martensite with the crystal structure of $Au_{23}Cu_{30}Zn_{47}$.

3.11. Summary of Landau model

Let in now summarize the essentials of the Landau model. It is in some sense a semi-microscopic model since it is made for describing single crystals containing very many atoms without defects if the applied shear stress has a definite orientation.

The model obviously applies to single crystallites of polycrystalline material. This means that for polycrystals the model works on a microscopic level compared with the dimension of the body. It may serve as a base for dealing with polycrystals in the same sense as the theory of anisotropic elasticity serves as a base for dealing with real poly-

crystalline material containing defects. To this end an averaging process over the single crystallites has to be performed. We can expect that the resulting mean constitutive relation has the same character as the Landau model suggests for the crystallites, yet with modified parameters which may be measured directly.

The Landau model substantially is nonlinear to such an extent that even unstable domains exist. To my knowledge very little is known about the elasticity theory of such materials. Some considerations in this direction have recently been made by ERICKSEN [11], JAMES [12], and PARRY [13].

From the point of view of the catastrophy theory, the Landau model is an example for the butterfly catastrophe whereas the liquid-vapour phase transition corresponds to the much simpler cusp catastrophe.

To finish this part I wish to emphasize that the aim of the model is not to give exact quantitative results but to reflect the behaviour of shape memory alloys qualitatively. It allows for deriving the whole variety of phenomena observed in these alloys from one simple free energy function.

4. Ginzburg–Landau theory of the one-dimensional model

4.1. Free energy

In the Landau theory we build up the crystal by stacking crystal layers with slowly varying strain along the stacking direction. In this way we get a deformed crystal without phase boundaries. In the Ginzburg–Landau theory we give up this restriction and allow for rapidly varying shear.

In the Landau theory the free energy density F_L at a point x depends on the strain at the point x (Eq. (3.1)). In the Ginzburg–Landau theory we add a term which depends on the gradient of the strain at that point which is a measure of lattice curvature. This term is beyond the scope of the classical nonlinear theory of elasticity. The simplest possibility of adding a curvature term is chosen here, namely, the gradient of the strain squared with a constant coefficient δ. A linear term cannot occur because of symmetry. We have

$$(4.1) \quad F(x, t) = F_L\big(\varepsilon(x), t\big) + \delta\left(\frac{d\varepsilon}{dx}\right)^2 = \alpha\varepsilon(x)^6 - \beta\varepsilon(x)^4 + \gamma(T-T_1)\,\varepsilon(x)^2 + \delta\left(\frac{d\varepsilon}{dx}\right)^2,$$

$$\alpha, \beta, \gamma, \delta, T_1 > 0, \text{const.}$$

For convenience we rescale the variables F, ε and T as well as the coordinate x to get

$$f(\xi, t) = f_L\big(e(\xi), t\big) + e'^2 = e(\xi)^6 - e(\xi)^4 + \left(t + \frac{1}{4}\right)e(\xi)^2 + e'(\xi)^2,$$

$$(4.2) \qquad f = \frac{\alpha^2}{\beta^3}\, F, \quad e = \sqrt{\frac{\alpha}{\beta}}\,\varepsilon, \quad e' = \frac{de}{d\xi}, \quad \xi = \sqrt{\frac{\beta^2}{\alpha\delta}}\, x,$$

$$t = \frac{\alpha\gamma}{\beta^2}\,(T-T_1) - \frac{1}{4}.$$

The response of the system to deformation is twofold. Firstly we have the stress σ which is the response to strain:

$$(4.3) \qquad \sigma = \frac{\partial f}{\partial e} = \frac{\partial f_L}{\partial e} = 6e^5 - 4e^3 + 2\left(t + \frac{1}{4}\right)e,$$

σ is the same as in the Landau theory (Eq. (3.5)). Secondly we have the couple stress μ which is the response to a lattice curvature e'

$$(4.4) \qquad \mu = \frac{\partial f}{\partial e'} = 2e'.$$

In this special form of the free energy the couple stress is linear in the lattice curvature and depends only on the curvature itself. It does not depend on strain and temperature. The equations for σ and μ are the constitutive equations or equations of state.

4.2. Conditions of equilibrium

The total free energy results from integrating the free energy density over the stacking direction

$$(4.5) \qquad f_{tot}(t) = \int_{\xi_1}^{\xi_2} f(\xi, t)d\xi,$$

ξ_1 and ξ_2 are the boundaries of the system.

Deriving the equations of equilibrium, we restrict ourselves to the case in which no external load is applied. The one-dimensional model has the disadvantage that a surface load can be applied only if a volume force is applied, too, which compensates the torque of the former.

If there is no external load, the equilibrium configuration is determined by the minimum of the total free energy with respect to a variation of the strain. After some calculation we get the equations of equilibrium:

$$(4.6) \qquad \begin{aligned} \sigma - \mu' &= 0 \quad \text{in the interior,} \\ \mu &= 0 \quad \text{at the surface.} \end{aligned}$$

Inserting the constitutive equations (4.4) and (4.3) into the equations of equilibrium (4.6), we get the field equations:

$$(4.7) \qquad \begin{aligned} 6e^5 - 4e^3 + 2\left(t + \frac{1}{4}\right)e - 2e'' &= 0 \quad \text{in the interior,} \\ e' &= 0 \quad \text{at the surface.} \end{aligned}$$

The field equations always have the simple solution $e = e_0 = $ const. The constant strain is such that the stress vanishes. This means we have unstressed austenite ($e = 0$) or martensite (e_0, Eq. (3.4)) corresponding to the minima of the Landau free energy f_L. This solution is trivial but it always gives us the absolute minimum of the total free energy.

4.3. Structure of domain walls

If $t < 1/12$, that is if the Landau free energy has more than one minimum, there is an additional solution of the field equations corresponding to two coexisting phases which are separated by a domain wall.

To get this second solution, we integrate the field equation once:

$$(4.8) \qquad\qquad e' = \sqrt{f_L(e) - f_{L_0}}.$$

From the surface condition which says that the lattice curvature e' has to vanish at the surface, we find that the constant of integration f_{L_0} has the meaning of the Landau free energy of the surface points which has to be the same at either end.

We notice that in order to have a well-defined real curvature e', the Landau free energy of each point in the interior has to be not lower than the Landau free energy of the surface points. From Eq. (4.8) we can construct the shape of domain walls (Fig. 16). The structure of the walls depends on temperature since so does the Landau free energy.
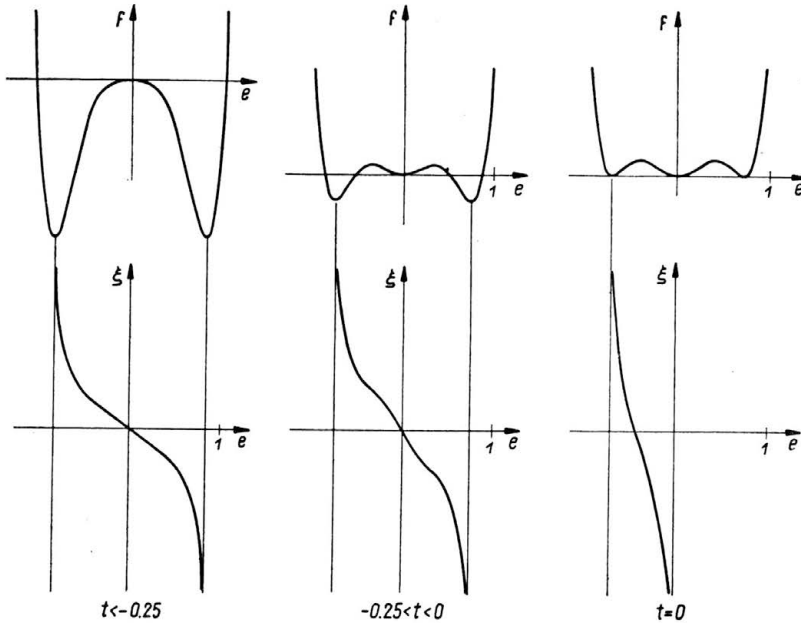

FIG. 16. Structure of domain walls in an infinite crystal as constructed from the Landau free energy function (Eq. (3.3), Fig. 4, upper part of this figure) with the help of Eq. (4.8). In the lower part the strain e across the wall (coordinate ξ) is plotted. The left two pictures correspond to a wall between martensite twins, the right picture corresponds to an austenite-martensite wall.

For $t < 1/4$ f_L has only martensitic minima. The domain wall between right and left martensite twin may be called kink in analogy to kinks in dislocation lines. In this temperature domain the Landau free energy is highest in the middle between the martensitic minima. Therefore the strain goes from one martensite valley to the other on a relatively straight way.

For $-1/4 < t < 0$ we have an additional austenitic minimum of the Landau free energy which is not so deep as the martensitic ones. Now the strain does not cross from left to right martensite twin in such a straight manner as before. In the region of the austenitic minimum it has a little delay. This means that the domain wall between the martensite twins includes a tiny sheet of austenite in this temperature domain.

If $t = 0$, all the minima are of equal depth. In this case we have a domain wall between austenite and martensite.

If $t > 0$, we cannot have a domain wall between martensite and austenite which both extend to infinity.

In order to have analytical results, we must integrate once more getting an elliptic integral, the evaluation of which strongly depends on the shape of the Landau free energy, that is on temperature.

$$(4.9) \qquad \xi(e) = \int \frac{de}{\sqrt{e^6 - e^4 + \left(t + \frac{1}{4}\right)e^2 - f_{L_0}}}.$$

For an infinite crystal the integral can be given by elementary functions:

$$e(\xi) = e_0 \left(1 + \frac{a}{\sinh^2 \lambda \xi}\right)^{-1/2} \operatorname{sgn} \xi, \qquad t < 0,$$

$$(4.10) \qquad \lambda = e_0 \sqrt{3e_0^2 - 1}, \qquad a = \frac{3e_0^2 - 1}{2e_0^2 - 1};$$

$$e(\xi) = e_0 (1 + e^{-2e_0^2 \xi})^{-1/2}, \qquad t = 0,$$

$$e_0 = \left(\frac{1}{3} + \frac{1}{6}(1 - 12t)^{1/2}\right)^{1/2} \qquad (\text{Eq. } (3.4)).$$

In this case we can easily calculate the width of the domain walls which is plotted in Fig. 17 as a function of temperature. The domain walls between the martensite twins become bigger and bigger the higher the temperature is. At $t = 0$ this boundary grows to infinity. In place of that the austenite-martensite domain wall gets stable.
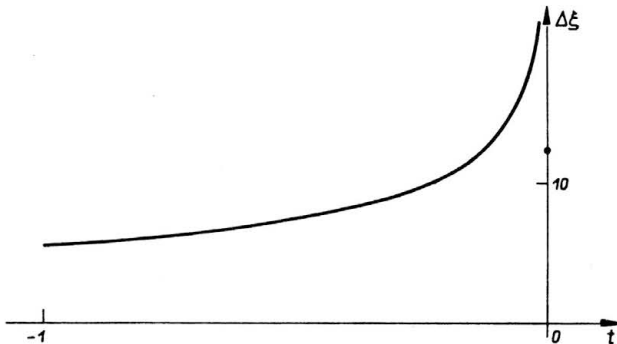

FIG. 17. Width of the domain wall between martensite twins over temperature. The width diverges for $t = 0$. In this case an austenite-martensite wall is stable, the width of which is marked by a dot.

4.4. Energy of the domain walls

Now the energy of a domain wall can be calculated. To this end the zero of energy has to be chosen in a way that at infinity, where we have undeformed martensite, the free energy is zero. Otherwise we would get an infinite energy. It is convenient to integrate with respect to strain instead of the coordinate ξ. Note that the mapping of e to ξ is one-to-one along a wall (Eq. (4.10)). We must remember that the free energy is added up by the Landau free energy, depending only on strain and temperature and by the lattice curvature squared (Eq. (4.1)). From the equation of equilibrium we know that the curvature squared equals the Landau free energy (Eq. (4.8)). Therefore we find that at each point of the wall in equilibrium half of the free energy comes from strain, the other half from lattice curvature. This fact simplifies the energy calculation considerably.

$$(4.11) \qquad f_{tot}(t) = \int_{\xi_1}^{\xi_2} f(\xi, t)d\xi = 2 \int_{-e_0(t)}^{e_0(t)} [f_L(e, t)/e']de =$$

$$= \frac{1}{2}\left[e_0 \sqrt{3e_0^2 - 1} + (2e_0^2 - 1)(6e_0^2 - 1)\ln \frac{e_0 + \sqrt{3e_0^2 - 1}}{\sqrt{2e_0^2 - 1}} \right],$$

$$t < 0 \qquad \text{martensite-martensite wall.}$$

$$(4.12) \qquad f_{tot}(t = 0) = \int_{\xi_1}^{\xi_2} df(\xi, 0)d\xi = 2\int_{0}^{e_0(t)} [f_L(e, 0)/e']de = \frac{1}{8},$$

$$t = 0 \qquad \text{martensite-austenite wall.}$$

We find that the free energy of a $M^+ - M^-$ wall decreases with increasing temperature nearly linearly (Fig. 18).
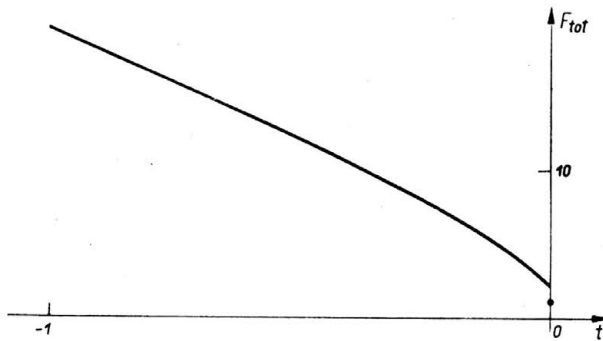
FIG. 18. Total free energy f_{tot} of the domain wall between martensite twins over temperature (Eq. (4.11)). The dot indicates the free energy of an austenite-martensite wall at $t = 0$ (Eq. (4.12)).

4.5. Determination of parameters

In the Ginzburg–Landau theory there are five parameters to fit the theory to a specific material (Eq. (4.1)). Four parameters, namely $\alpha, \beta, \gamma, T_1$, are the same as in the Landau theory. The fifth one, δ, is an additional parameter which is involved in the rescaling of

the coordinate x. To get this value from experiments, we can either take the width of the boundary or its energy. From experiments we know that the walls are very narrow, only some lattice parameters wide. Therefore a continuum theory like the Ginzburg–Landau theory can be taken as an approximation only. As an example, we may take as width 10 Å, which gives

$$\delta = 10^{-12} \text{ J/cm}.$$

With this value we get the energy of a wall in the order of magnitude of 10 erg/cm^2 which is typical for nonferrous alloys.

5. Analogy between the martensitic phase transition and other phase transitions

For ferroelectrics, DEVONSHIRE [14] suggested a Helmholtz free energy of the same type as Eq. (3.1). Ferroelectric materials show, depending on the material, a first or a second-order phase transition from the dielectric high temperature phase to the ferroelectric low temperature phase with different possibilities of orientation. There is a very close analogy between ferroelectrics and shape memory alloys [6, 7].

There is a somewhat looser analogy to ferromagnetic materials where the phase transition is of second order. In Table 1 the corresponding quantities of martensitic, ferroelectric, and ferromagnetic phase transitions are listed.

Table 1. Analogy between martensitic, ferroelectric, and ferromagnetic phase transitions.

Martensitic phase transition	Ferroelectric phase transition	Ferromagnetic phase transition
first order	first or second order (depends on material)	second order
austenite	dielectric phase	paramagnetic phase
martensite	ferroelectric phase	ferromagnetic phase
strain	polarization	magnetization
stress	electric field	magnetic field
equilibrium phase transition temperature at $\sigma = 0$	Curie temperature	Curie temperature
domain boundaries between martensite variants	ferroelectric domain walls	Bloch walls
elastic constant	1/electric susceptibility	1/magnetic susceptibility
Landau theory	Devonshire theory	mean field theory (P. Weiss)
Ginzburg–Landau theory		micromagnetic equations (W.F. Brown)

References

1. L. DELAEY, R. V. KRISHNAN, H. TAS, H. WARLIMONT, J. Mat. Sci., **9**, 1521–1555, 1974.
2. A. L. ROITBURD, Sol. St. Phys., **33**, 317–390, 1978.
3. A. L. ROITBURD, G. V. KURDJUMOV, Mat. Sci. Eng., **39**, 141–167, 1979.

6*

4. *Shape memory effects in alloys*, J. Perkins [ed.], Plenum Press, New York 1975.

5. F. Falk, ZAMM, **60**, T118–T120, 1980.

6. F. Falk, Acta met., **28**, 1773–1780, 1980.

7. I. Müller, K. Wilmański, Nuovo Cim., B57, 283–318, 1980.

8. K. Wilmański, Summer school on "Materials with shape memory", Jabłonna 1981.

9. C. Zener, Phys. Rev., **71**, 846–851, 1947.

10. Y. Murakami J. Phys. Soc. Jpn., **33**, 1350–1360, 1972.

11. J. L. Ericksen, Arch. Rat. Mech. Anal., **73**, 99–124, 1980; J. Elast., **5**, 191–201, 1975; J. Appl. Mech., **45**, 740–744, 1978.

12. R. D. James, Arch. Rat. Mech. Anal., **72**, 99–140, 1979; Arch. Rat. Mech. Anal., **73**, 125–158, 1980.

13. G. P. Parry, Int. J. Solids Struct., **16**, 275–281, 1980.

14. A. F. Devonshire, Adv. Phys., **3**, 85–130, 1954.

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