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## The Martensite Transformation

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The martensite transformation is, essentially, a deformation caused by the free energy difference of the austenite and martensite phases. It may be considered from two aspects. One concerns the structural relationships between the two phases, which are largely known and interpreted [1]. The other has to do with the transformation mechanism. It is this aspect of the martensitic transformation which is presently not entirely clear. Therefore, it will be considered in this paper.

The martensitic deformation strains may be almost infinitesimal, finite, homogeneous, or inhomogeneous in character. Consequently, all aspects of the theory of elasticity and plasticity enter into the interpretation of the transformation mechanism. Suggestions can be found which try to interpret the onset of the transformation in terms of an elastic instability [2 - 4], a dislocation instability [5 - 7], as well as an instability of various lattice waves of finite wavelength and amplitudes [8], or combinations thereof [9]. All these, and similar unnamed suggestions, address themselves to the mechanics of the transformation and not so much to the nature of the driving force. Since the nature of this force will determine the transformation mode, we will address ourselves to it in an effort to highlight what information about this force is currently lacking.

Consider a first order martensite transformation. Both the austenite and martensite are in equilibrium in the vicinity of the transformation temperature,  $M_S$ , as indicated in Fig. 1. This is the figure commonly used in discussions of phase transformations and its mechanisms. Its nature suggests that an expression of the free energy up to the fourth power, in one order parameter, be studied. In general, though, more than one order parameter will have to be considered, as exemplified by the

many different martensite phases in Fe-Mn-C alloys [10] among others. This observation leads to Fig. 2 which is reminiscent of the classical rate theory of diffusion [11] except that the abscissae now are order parameters instead of normal co-ordinates. The formulation of a rate theory of the martensite transformation will then proceed along the lines of classical diffusion theory if it can be assumed that order parameters and normal co-ordinates are equivalent.

A consideration of the complete space spanned by all order parameters raises the question as to whether it is necessary to in-

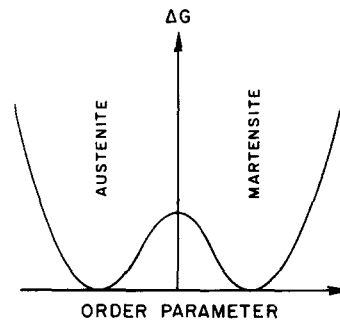


Fig. 1. Free enthalpy of austenite and martensite at the  $M_S$  temperature. Only one order parameter, a deformation parameter is considered.

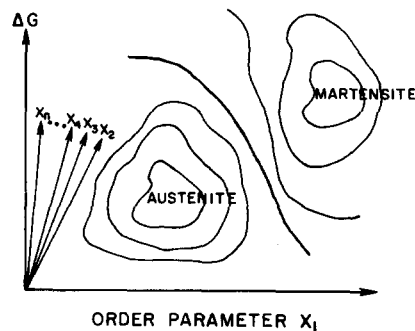


Fig. 2. Free enthalpy of austenite and martensite, many order parameters considered.

clude into the theory of the martensite transformation the coupling between order parameters. This appears to be essential if one wants to understand the pre-martensitic fluctuations observed by neutron scattering [12, 13] as well as electromicroscopically [14 - 17]. As these fluctuations will lead eventually to the transformation proper, their understanding is of central importance. In the following, therefore, we will discuss some consequences of the coupling mechanism.

The simplest situation arises if only two-order parameters need be considered. One of them has to be a deformation parameter, the other one need not be. The consequence of the coupling can be explored most easily in a quasiharmonic approximation. In this approximation, the free energy,  $\Delta G$ , is given by

$$\Delta G(x_1, x_2) = A_{11}x_1^2 + A_{12}x_1x_2 + A_{22}x_2^2. \quad (1)$$

In eqn. (1), the  $x_i$  denote the two order parameters and the  $A_{ij}$  are coefficients which only depend on an external variable such as temperature, magnetic field or pressure. The corresponding equations of motion of the coordinates,  $x_i$ , of the point representing the phase on the  $\Delta G$  surface are now coupled and, hence, its motion is modulated. The modulation leads to a phenomenon which has as its analog the self-trapping distortion controlling interstitial diffusion [18]. It is thus possible that the martensite transformation proceeds in a self-sustaining fashion.

Return to Fig. 1. When discussing the martensite transformation in terms of it, hence, only in terms of one-order parameter and rate theory, it is assumed that the potential varies with time as shown in Fig. 3(a). Other ways in which the potential may change are presented in Fig. 3(b) and (c). Figure 3(c) corresponds to the self-trapping mechanism by which the parent austenite "digs" itself through the potential barrier. Superimposed on the vibrations, the frequency of which are given by the curvature of the local potential, we may find interphase oscillations of longer duration, leading to periodical changes of the position of the minimum. Such an oscillatory pattern corresponds to the coupling mechanism envisaged in the previous paragraph if the eigen frequencies of the two order parameters are sufficiently different.

The mechanism shown in Fig. 3(c) has been suggested for the martensitic transformation

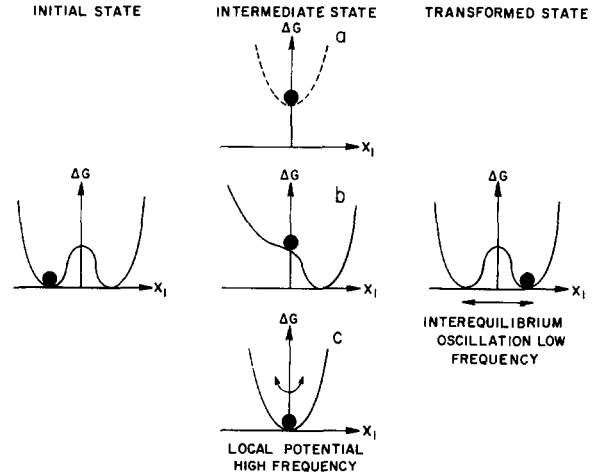


Fig. 3. Different intermediate stages in the course of the martensite transformation: (a) reaction rate theory, the activated state is treated like an equilibrium state; (b) the activated state is not an equilibrium state; (c) self-trapping mechanism, the system is always in equilibrium. Note that the abscissae for the second order parameter has been omitted.

in  $\text{Nb}_3\text{Sn}$  and  $\text{V}_3\text{Si}$  [19], as well as many insulators [20]. For the two alloys it has been suggested that the second-order parameter be given by the Jahn-Teller splitting of the degenerate  $3d$  band at the center of the Brillouin zone as both transformations are uniform. Since the self-trapping mechanism is conceptually capable of interpreting the low frequency pre-martensitic oscillations observed in a variety of materials, it might well be generally operative. Indeed, a coupling mechanism has already been mentioned in connection with the  $\omega$ -transformation [21].

The splitting of degenerate electron energy levels is proportional to the applied or fluctuating field. Since one of the split bands will be shifted to lower energies by the splitting, the constant,  $A_{21}$ , in eqn. (1) will be negative [22]. The constant,  $A_{11}$ , in the same equation will be, in general, positive, since in most cases all phonon frequencies remain finite at the martensite start temperature [23]. As the experimental evidence further indicates that the deformation order parameter changes faster with time than the other order parameter [13 - 15], eqn. (1) becomes for small times

$$\Delta G(x_1, t) = -A'_{12}x_1(t) + A_{11}x_1(t)^2$$

where

$$A'_{12} = A_{12}x_2, \quad x_2 \simeq \text{const.}$$

Local equilibrium is thus attained at a finite deformation,

$$x_1(t) = A'_{12}/2A_{11},$$

and the position of the minimum varies approximately as  $\dot{x}_2 \neq \dot{x}_1$ , in qualitative agreement with the mechanism depicted in Fig. 3(c). It should be noted that this mechanism, in principle, obviates the need for a separate discussion of the stability of the parent austenite with regard to small and large fluctuations of the order parameter.

The coefficient  $A_{12}$  in eqn. (1) represents a many-body-force driving the martensitic transformation. Other possibilities exist, however. It can be assumed, for instance, that the gradient energy provides the driving force [24, 25]. In this case, the inclusion of higher order terms in the expression for  $\Delta G$  becomes essential, and the transformation is necessarily of first order. The transformation proceeds by distorting initially sinusoidal, large amplitude lattice waves of comparatively large wavelength. As the distortion grows, periodic modulations occur which represent a dynamic martensite nucleus. The essence of this mechanism is that the kinetic energy of the lattice wave becomes concentrated in certain regions facilitating their co-operative activation [25]. In general, a combination of the two mechanisms will be operative.

Most martensitic transformations are not characterized by a volume instability, they are heterogeneously nucleated. One might thus ask what character such a nucleus has in terms of the two mechanisms sketched above. There will be "electronic" and "mechanical" nuclei. The former are represented by regions in the crystal where the electronic degeneracies are already split, *i.e.*, by defects of symmetry lower than that of the austenite. This includes many point defects, all dislocations, interfaces and surfaces. The latter must provide the large amplitude lattice wave, *i.e.*, it is a point, line, or planar defect without symmetry restriction. Either nucleus is in a sense "invisible" and "autokatalytic" and we thus rediscover a previous suggestion [26].

The foregoing paragraphs contain the framework of a theory of the initial stages of martensite formation conceptually applicable to all metals and alloys. In its simplest form, it applies to certain almost second-order martensites. In general, other coupling mechanisms

such as spin-orbit [27] or magnetoelastic [28] coupling must be considered, and higher order terms in *all* order parameters must be included in the series expansion for  $\Delta G$ . Such higher order terms are conceptually necessary for first order transformations. Quantitatively, their importance can only be assessed if the nature of the predominant driving force is known. The lack of knowledge of this driving force for classical martensites presently precludes such an assessment, and it is probably in this area where we find our knowledge about the martensite transformation most wanting. Does the Jahn-Teller splitting or the gradient energy provide the predominant driving force? Are both forces independent of each other? If the Jahn-Teller splitting is operative, which degeneracies are split? Degeneracies inherent in the symmetry of the Brillouin zone or accidental degeneracies? Where are such degeneracies located? In short, information about the electronic structure of austenite is lacking. This statement might be surprising in view of the efforts made to obtain such information. It must be recalled, though, that only small segments of the Fermi surface will be affected by the splitting. Therefore, we can summarize by saying that "We do not know small but important details of the electronic structure of the austenite which control the martensite transformation".

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