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INTRODUCTION

Recently there has been a resurgence of interest in the effect of the martensitic phase transition which occurs in many A15 compounds[1] on superconductivity[2] and on elastic and anelastic behavior.[3] Since in many practical applications, A15 compounds are subject to considerable stress and strain, it is of interest to examine the interaction of stress with the martensitic transition; this paper is an examination of the effects of stress predicted by a simple Landau model which successfully describes many features of the transition and the related temperature dependence of the elastic modulus $(c_{11}-c_{12})/2$.[1] Earlier, Pietrass[4] has discussed some of the effects of stress on the phase transition, in the context of a Landau model, and the present paper is an extension and development of this theoretical approach. We will focus on the effect of stress on the temperature ranges of stability and metastability of various types of martensitic domain and will briefly discuss the non-linearity of the stress-strain relation in a polycrystalline A15.

SYMMETRIZED STRESSES AND STRAINS

The lattice distortions associated with various types of martensitic domain and the effect of different types of stress are most efficiently characterized in terms of symmetrized linear

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combinations of strain components e_{xx}, e_{yy}, etc. (relative to cubic crystal axes x, y, z):

$$e_1 = (2e_{zz}-e_{xx}-e_{yy})/\sqrt{6} \tag{1}$$

$$e_2 = (e_{xx}-e_{yy})/\sqrt{2} \tag{2}$$

$$e_v = (e_{xx}+e_{yy}+e_{zz})/\sqrt{3} \tag{3}$$

with symmetrized stress components similarly defined. In a linearly-elastic cubic phase, e_1 couples only to σ_1, e_2 only to σ_2, and e_v only to σ_v. However, in a martensitically transforming A15, nonzero values of e_1 and e_2 arise below the transition temperature T_m due to the tetragonal lattice strain of the transition. The relative values of e_1 and e_2 in a transformed domain depend on whether the tetragonal axis is parallel to the x, y, or z axis: in a stress-free crystal $(e_1,e_2) = (e,0)$ in a z-domain, $(-e/2,\sqrt{3}e/2)$ in an x-domain, and $(-e/2,-\sqrt{3}e/2)$ in a y-domain, where e varies with temperature. The values of the symmetrized stress components in a crystal depend on the orientation of the crystal axes relative to the principal stress axes; for example, in a cylindrical filamentary composite the values of σ_1 and σ_2 in a given crystallite are $(\sigma_L-\sigma_R)(3n_z^2-1)/\sqrt{6}$ and $(\sigma_L-\sigma_R)(n_x^2-n_y^2)/\sqrt{2}$ respectively, where σ_L and σ_R are the longitudinal and radial stress components and n_x, etc., are the direction cosines between the crystal axes and the longitudinal axis of the composite. Thus, for general orientations σ_1 and σ_2 both have nonzero values, although certain experiments such as x-ray measurements may select crystallites whose orientation yields only nonzero values of σ_1; for example, all crystallites with the crystal z-axis parallel to the filament axis have $\sigma_2=0$.

A SIMPLE MODEL

The simplest model which illustrates the essential features of the interaction of stress with the transition is a simple Landau model[1] in which the free-energy density relative to the cubic phase is:

$$F = \frac{1}{2}Ae_1^2+\frac{1}{4}Ce_1^4-\sigma_1 e_1 \tag{4}$$

where $A=(c_{11}-c_{12})$ is a function of temperature, and C is sensibly independent of temperature. Near the transition temperature A varies essentially linearly with temperature, and Weger and Goldberg[1] showed that the elastic properties of a Nb_3Sn single crystal can be described accurately over a wide range of temperature with a temperature dependence of the form:

$$A(T) = A'[T-T^*]\{(1+a_\infty^2)/[(T/T^*)^2+a_\infty^2]\}^{1/2} \quad (5)$$

where A' and a_∞ are constants and a_∞ is chosen to give the correct ratio of the modulus ($c_{11}-c_{12}$) at low and high temperatures ($a_\infty \approx 1$ for Nb_3Sn). The equilibrium strain at fixed T and σ_1 is obtained from $\partial F/\partial e_1=0$. Typical results are shown in Fig. 1; the essential features are easily obtained from the properties of quadratic and cubic equations.

The results shown in Fig. 1 illustrate the main properties of the simple model. With no applied stress there is a second-order phase transition at T^* (a model for which the transition is first order will be discussed below) from a cubic phase to one of two

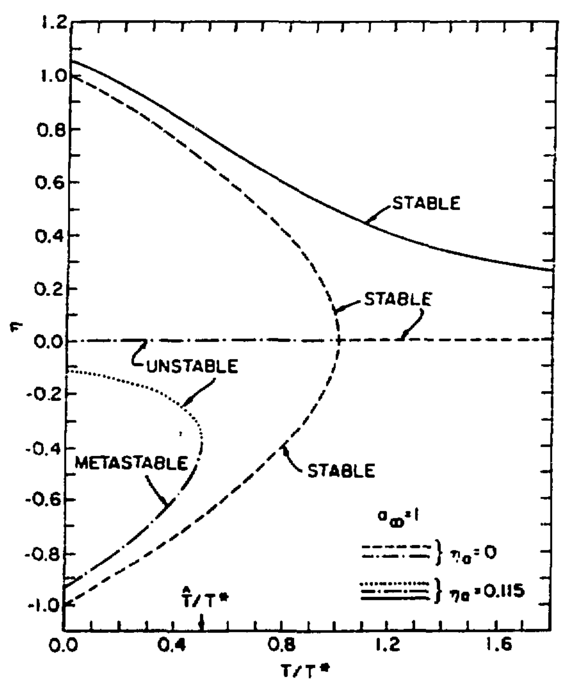

Fig. 1. Effect of applied stress on values of strain for which $\partial F/\partial e_1=0$, F given by equation 4. $\eta \equiv e_1(T,\sigma_1)/|e_1(0,0)|$. Applied stress is expressed as an equivalent strain at high temperature: $\eta_a \equiv \sigma_1/[A(T\to\infty)|e_1(0,0)|]$. The temperature dependence of the modulus $A=(c_{11}-c_{12})$ is that of equation 5 with $a_\infty=1$.

degenerate tetragonal "ferroelastic" phases with tetragonality of opposite sign. For illustrative purposes we can regard the phase with positive e_1 as a z-domain and the phase with negative e_1 as a composite of an x- and a y-domain. The application of a σ_1 stress "parallel" to the tetragonality of the z-domain (i.e. with the same sign as e_1 for the z-domain) has several consequences: i) the sharp second-order transition is replaced by a continuous, diffuse transition between "paraelastic" and "ferroelastic" states; ii) the degeneracy in energy of the z- and the xy-domains is removed with the z-domain being thermodynamically stable while the xy-domain becomes metastable; iii) the temperature of the continuous transition, as measured by the location of the inflection point $\partial^2 e_1/\partial T^2=0$, is independent of stress, remaining pinned at T^*; and iv) the temperature, $\hat{T}$, above which the metastable domain becomes absolutely unstable is depressed, steeply at first, by increasing σ_1, $\hat{T}$ being given by the condition $A(\hat{T})=-[(27/4)C\sigma_1^2]^{1/3}$. Taking the temperature dependence of A given in equation 5 yields the results shown in Fig. 2.

A MORE REALISTIC MODEL

The most serious deficiencies of the simple model above are: i) it exhibits a second- rather than a first-order transition accompanied by a small strain discontinuity, as is actually the case for V_3Si and Nb_3Sn[1]; and ii) it does not properly distinguish between

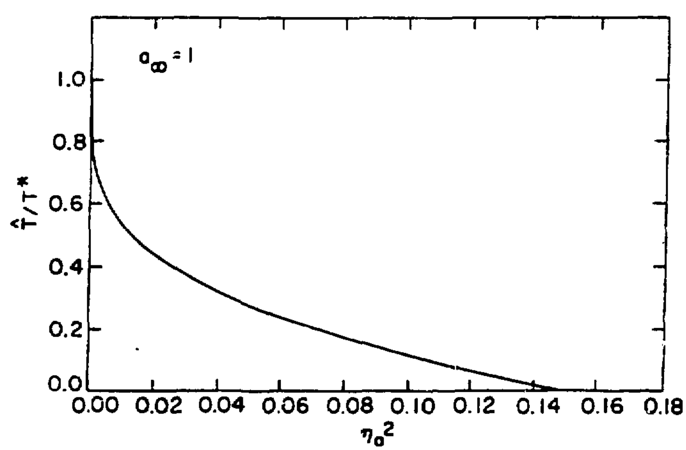

Fig. 2. Temperature above which metastable domains become absolutely unstable. Nomenclature is as in Fig. 1.

x-, y-, and z-domains. The first deficiency is removed by including a small term cubic in strain in the free-energy density (equation 4); the strain for which $\partial F/\partial e=0$ is then of the form shown in Fig. 3 rather than that in Fig. 1. The second deficiency is remedied by including the symmetrized strain component e_2 as well as e_1 (see equations 1 and 2).

Pietrass[4] has described a free-energy density function with the correct symmetry; neglecting a small coupling between hydrostatic strain and the martenistic transition this becomes:

$$F = \frac{1}{2}A(e_1^2+e_2^2)+\frac{1}{3}Be_1(e_1^2-3e_2^2)+\frac{1}{4}C(e_1^2+e_2^2)^2-e_1\sigma_1-e_2\sigma_2 \qquad (6)$$

where A and C are as described previously, and B is assumed to be sensibly independent of temperature. For fixed T, σ_1, and σ_2 equilibrium strains are found by simultaneously solving $\partial F/\partial e_1=0$ and $\partial F/\partial e_2=0$; in general this must be done numerically. However, if we restrict consideration to only nonzero σ_1 stresses, the essential

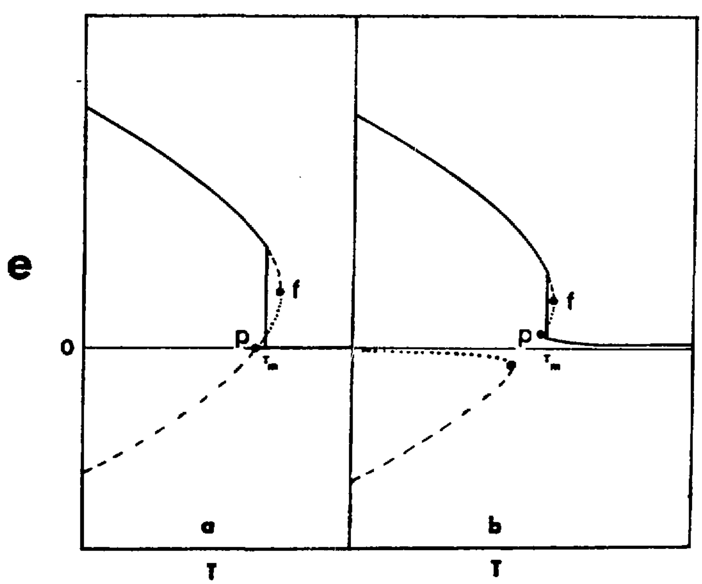

Fig. 3. Values of strain e at which $\partial F/\partial e=0$ for a Landau model, including terms cubic in strain. In a) $\sigma_1=0$ and in b) $\sigma_1\neq0$. Stable phase ——; metastable phase ---; absolutely unstable ... . Points p and f mark respectively the onset of instability in the "paraelastic" or cubic phase and the "ferroelastic" phase.

features can be derived analytically, and we can thus obtain a qualitative understanding of the interaction of the stress with the transition. (The basic effect of nonzero σ_2 is to lift the energetic degeneracy of x- and y-domains.) However, our previous discussion shows that $\sigma_2=0$ only for crystallites of special orientation in, for example, a filamentary conductor.

When a stress σ_1 with the <u>same</u> sign as e_1 in a transformed z-domain is applied, the effect at low stresses is: i) to raise the temperature of the transition between the distorted cubic (paraelastic) phase and a ferroelastic z-domain and simultaneously to reduce the discontinuity at the transition, as shown in Fig. 3; and ii) to make the x- and y-domains metastable, with a simultaneous reduction in the temperature of the onset of instability (the point f of Fig. 3). The amount of these changes at small stress is $\Delta T_m \simeq +2\sigma_1/A'e_m$ and ΔT_f(x- or y-domain)$\simeq -2\sigma_1/3A'e_m$ where $e_m \equiv -2B/3C$ is the spontaneous change in e_1 at the transition and A' is as in equation 5. As the stress increases, the points p and f in Fig. 3 move closer together; at the point of coalescence the first-order character of the transition has been destroyed, and thereafter the strain vs T curve resembles that of Fig. 1. The critical applied stress for this event is $\sigma_{crit}=Ce_m^3/8$. This condition may be expressed more understandably as a critical value of the equivalent normalized applied <u>strain</u> (defined in the caption of Fig. 1): $\eta_a^{crit} \simeq e_m(B^2/A'C)/[18T^*|e_1(0,0)|]$. For typical values[1,4] of the various parameters of Nb_3Sn, $\eta_a^{crit} \simeq 0.003$: an applied strain of only $\sim$0.3% of the spontaneous strain at $\sigma_1=0$ and T=0 serves to destroy the first-order character of the transition. The concommitant temperature rise at the critical stress is only about 0.5-0.8 K. For larger stresses, the temperature of the diffuse transition, as measured by the inflection point in the e_1 vs T curve, rises slowly with stress, given by $A(T_{i.p.}) = 3e_m(C^2\sigma_1)^{1/3}/2$ and equation 5.

When a stress σ_1 of sign <u>opposite</u> to that of e_m is applied, at low stresses a first-order transition from the tetragonal paraelastic phase to a ferroelastic x- or y-domain occurs; the symmetry of the ferroelastic domain distorted by the stress is orthorhombic. Initially, the transition temperature rises at a rate given by $\Delta T_m \simeq -\sigma_1/A'e_m$. As before, at a critical value of the stress, $\sigma_{crit} = -81Ce_m^3/128$, the first-order character of the transition is destroyed and the transition is continuous thereafter. (This critical stress is equivalent to a strain at high temperatures of only $\sim$-1.5% of the spontaneous strain at $\sigma_1=0$ and T=0.) Unlike the previous case ($\sigma_1 e_m>0$), a change of symmetry from tetragonal to orthorhombic occurs at the temperature of the continuous transition when $\sigma_1 e_m<0$. The temperature of the continuous transition, given by $A(T_{ct}) = 2B(\sigma_1/3B)^{1/2}-C(\sigma_1/3B)$ and equation 5, passes through a <u>maximum</u> value which is higher than the unstressed transition temperature by $\sim(7/9)(B^2/A'C)\{1+[(B^2/A'C)/T^*(1+a_s^2)]\}$ or only by about 3-5 K for V_3Si and Nb_3Sn. Finally, for a stress with $\sigma_1 e_m<0$, z-domains are metastable and the stress reduces the temperature of the onset of instability by $\Delta T_f \approx [-e_m \sigma_1^{1/3} C^{2/3} - (27 C \sigma_1^2/4)^{1/3}]/A'$ for stress larger than σ_{crit}.

NONLINEAR STRESS-STRAIN RELATIONS

The physical phenomena which give rise to the martensitic phase transition also give rise to important nonlinear terms in the stress-strain relation, above and beyond the normal anharmonic and plastic flow effects occurring in most materials. In principle such nonlinearity must be accounted for in computing the thermoelastic stress state of composite conductors. Landau models of the phase transition include strong nonlinear stress-strain effects. This can be seen in Fig. 4, which shows the normalized strain, η, as a function of temperature for various levels of applied stress, as calculated with the "simple model" embodied in equation 4. If the system were linear, the strain at high temperature, denoted as η_∞ in the figure, would equal the effective applied strain η_a; however it clearly does not, and the importance of nonlinear effects is largest near the transition temperature.

A more realistic description of the stress-strain relation can be derived from equation 6, with σ_1 obtained from $\partial F/\partial e_1$ and σ_2 from $\partial F/\partial e_2$. Thus, for example, the stress σ_1 arising from a pure tetragonal strain e_1 applied to a single crystal is:

$$\sigma_1 = A(T)e_1 + [(-3e_m/2) + e_1]Ce_1^2 \qquad (7)$$

where $e_m = -2B/3C$ is the spontaneous strain at the temperature of the phase transition; the second term is the nonlinear contribution. In actual conductors the A15 compound is present as a polycrystalline aggregate with the individual crystallites being oriented at random with respect to the principal axes of stress and strain (the specimen axes). It is straightforward, on the assumption that the strain throughout the polycrystal is constant, to calculate the resulting stress state in a crystallite of arbitrary orientation, and average over orientation to obtain the average stress; this is equivalent to the Voigt polycrystal average of elastic moduli.[5] It is much more difficult to obtain the average strain accompanying an assumed constant stress state, the equivalent of the Reuss polycrystal average of elastic constants,[5] since this involves solving coupled cubic equations. We conclude by presenting the "Voigt-averaged" stress in a random polycrystalline aggregate (each crystallite of which obeys equation 6 as well as the usual Hooke's law for shear strains of the "c_{44} type") subjected to a pure tetragonal strain e_I (see equation 1), referred to specimen axes, such as is present due to differential thermal contraction in a cylindrical composite conductor:

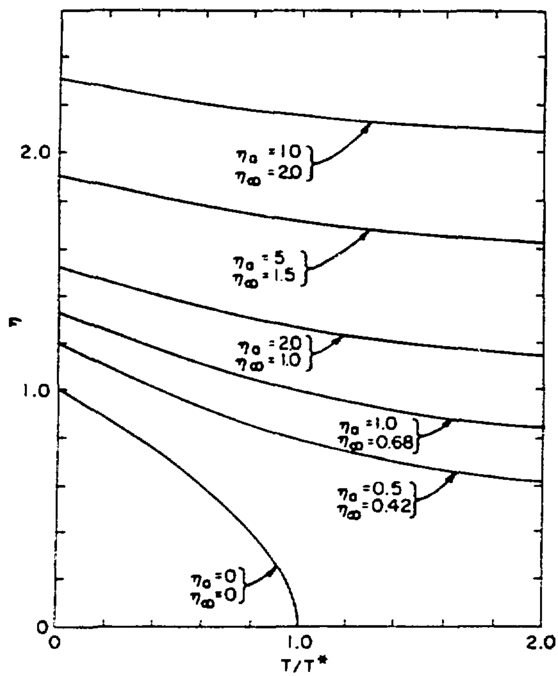

Fig. 4. Normalized strain in the thermodynamically stable state for the model described by equation 4. The effective applied strain, η_a, is defined in the caption of Fig. 1. η_∞ is the limit of η as $T \to \infty$ and would equal η_a if the system were linearly elastic.

$$\sigma_1)_{avg} = [2A(T)+6c_{44}]e_I/5+[(-12e_m/5)+(3e_I/10)]Ce_I^2 \qquad (8)$$

In principle such an equation should replace Hooke's law of linear elasticity in estimating the thermoelastic stress state in a composite conductor.

CONCLUSIONS

Analysis of Landau models[1,4] of the type which have successfully described a number of features of the martensitic phase transition and elastic softening in A15 compounds shows that the principal effect of applied stress in such models is to destroy the sharp transition, which is replaced by a smooth continuous transition, for stresses in excess of a rather small critical stress (which, expressed as an effective strain, is only a few percent of the spontaneous strain at T=0 accompanying the transition). The temperature of the transition is shifted by stress by at most a few degrees. Stress lifts the degeneracy in energy of domains with their tetragonal axis along different <100> directions and depresses the temperature at which metastable domains become unstable. Strong nonlinear stress-strain behavior is a feature of the Landau models and should be included in estimates of the thermoelastic stress state of composite conductors.

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