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A Model of Shape Memory Materials with Hierarchical Twinning: Statics and Dynamics

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We consider a model of shape memory materials in which hierarchical twinning near the habit plane (austenite-martensite interface) is a new and crucial ingredient. The model includes (1) a triple-well potential (ϕ^6 model) in local shear strain, (2) strain gradient terms up to second order in strain and fourth order in gradient, and (3) all symmetry allowed compositional fluctuation-induced strain gradient terms. The last term favors hierarchy which enables communication between macroscopic (cm) and microscopic (Å) regions essential for shape memory. Hierarchy also stabilizes tweed formation (criss-cross patterns of twins). External stress or pressure modulates ("patterns") the spacing of domain walls. Therefore the "pattern" is encoded in the modulated hierarchical variation of the depth and width of the twins. This hierarchy of length scales provides a related hierarchy of time scales and thus the possibility of non-exponential decay. The four processes of the complete shape memory cycle—write, record, erase and recall—are explained within this model. Preliminary results based on 2D molecular dynamics are shown for tweed and hierarchy formation.

I. INTRODUCTION

A variety of minerals, ceramics, ferroelectrics, Jahn-Teller materials, and most notably the shape memory alloys (e.g. NiTi, FePd, $CuAuZn_2$) undergo a diffusionless, displacive (i.e. martensitic), weakly first order structural transition and exhibit transformation precursors that can occur up to 100s of degrees above the transition temperature T_o. Many types of pretransitional structures (or "mesoscopic textures") have been observed in transmission electron microscopy (TEM) including the so called "tweed" (criss-cross pattern of twins) patterns [1,2]. It is widely accepted that the precursor behavior cannot be attributed to phonon mode softening, critical fluctuations, defects or impurities. In addition, it has gradually become apparent that precursors in martensites are intrinsic features indicative of stable (or metastable) modulated phases and that they are not due to artifacts developed in the course of the nucleation process. These materials also exhibit twinning below T_o. The twins are stabilized by a long range, habit plane linked, elastic interaction [3,4].

Martensite is a mesoscopic structure, a texture that occurs at a scale between atomic and macroscopic. The interphase boundaries involve 10 to 100 unit cells whereas the twinning and tweed modulation scale is microns. The multiscale phenomena or "martensitic" characteristics are now being observed in a variety of other materials, e.g. high T_c superconductors [5], magnetostrictive materials, etc. Our focus is on ferroelastic martensites that exhibit the **shape memory effect** (SME) and are technologically useful, e.g. in temperature control, actuators, transducers, etc. [6]. Finally, we note that both tweed and twins of varying length scales have been observed experimentally [1,2]. There is growing belief that these precursors are in some way responsible for shape recovery, but the mechanism of SME remains unclear.

The modulated phases can be understood quite generally within a Ginzburg-Landau framework if, in addition to the traditional elasticity terms, one appends appropriate nonlinear and nonlocal (strain gradient) terms to the elastic energy functional [7]. There are at least two models for tweed in the literature: (a) A static model based on T_o fluctuations induced by random local alloying (composition) fluctuations [8]. The criss-crossing domain walls forming the tweed are thus random local metastable minima in a quenched spin glass like picture [8]. Although this model captures a specific property of these materials, namely sensitivity of T_o to compositional fluctuations, there is no obvious narrow "window" of elastic constants/material properties, within which only the small class of martensitic materials would naturally fall. Disorder is an essential aspect of the model i.e. a perfect alloy would not show tweed. Furthermore, it is not obvious how the interesting property of shape memory involving macroscopic "write/record/erase/recall" cycle would enter these glassy models. (b) The second model is a kinetic nucleation model based on long range strains (included at a mean field level) induced by vacancies/defects in the lattice [5]. Tweed in this picture appears as a saddle point microstructure (either short lived or metastable) related to a temperature quench. This model has been shown in kinetic simulations to generate tweed as an intermediate (unstable or metastable) state over a limited range of time steps, while observed tweed is apparently a long lived microstructure. Neither of these models has any obvious property that would serve as a mechanism for the macroscopic "stress-temperature" cycle that constitutes the shape memory effect.

Here we present a phenomenological elastic model, quadratic in the strain and quartic in strain gradients, with all symmetry allowed terms consistently retained [9]. The model synthesizes a variety of properties specific to these materials. It contains two key ingredients, namely a cross-derivative gradient term that favors domain wall crossing, and the idea of hierarchical (e.g. Cayley tree) splitting of the domain walls from atomic scales at the habit plane to macroscopic scales inside the tweed. The tweed is obtained as a free energy minimum and its existence is here demonstrated in 2D simulations. Preliminary results based on a square-rectangle transformation indeed show a tweed with varying length scales.

II. HIERARCHICAL TWINNING MODEL

We construct below a phenomenological elastic model that synthesizes several ideas specific to these materials that have been suggested in the literature. Clapp has noted that the softness of martensitic materials implies that the coefficient of the quadratic strain gradient terms in the elastic energy $\sim a(\nabla\epsilon)^2$ may be small or even negative requiring higher order gradients $\sim (\nabla_x^2 + \nabla_y^2)^2$ to provide stability to the phonon spectrum [10]. Thus, one must consistently keep terms fourth order in gradient and quadratic in strain. We note that this, however, implies that one must also keep the symmetry allowed term (under 2D square-rectangle transformation) $\sim(\nabla_x^2 - \nabla_y^2)^2$. This clearly generates cross terms $-\nabla_x^2\nabla_y^2$ with a negative sign implying that criss-cross domain walls are energetically favored. Note that a similar term is generated by a Gaussian integration of compositional fluctuations linearly coupled to $\nabla_x^2\nabla_y^2$ [8]. The first key aspect of this model is the assumption that the renormalized coefficient of this term retains a negative sign. This enables a competition with elastic terms with positive coefficients in some range of elastic parameters.

The second key aspect is the idea of a hierarchical structure of domain walls at the habit plane. It is the energy lowering contributions of the negative cross gradient term from the hierarchical structure that eventually stabilize the tweed microstructure. The physical basis for twinning at a habit plane is that while the equilibrium strain of austenite is zero, that of only one variant of martensite is nonzero, implying unacceptably high elastic energies. Therefore, martensitic twinning, i.e. generating alternate "slabs" of positive and negative strain, leads to zero average strain over neighboring macroscopic twin widths. Kohn and Müller carried this idea further by proposing a domain wall twinning pattern even lower in energy with a branching of martensitic slabs into progressively finer widths as the habit plane is approached, resulting in zero strain when averaged over a few atomic spacings [11].

Our proposed hierarchy involves Cayley tree branching of *domain walls* rather than Kohn and Müller slabs, but incorporates the idea of zero atomic scale average strain on either side of the habit plane. Given these two key ideas in conjunction with a ϕ^6 type (i.e. triple well) model and appropriate gradient terms as above, one can show a minimum of free energy in terms of tweed size L and spacing W. The tweed region ends on the habit plane in a "skin" of hierarchical blocks attached to each domain wall. This is consistent with experimental observations [2] that show tweed like regions of varying scales. Our simulations on a discrete NxN lattice confirm this. It is also found that tweed microstructures are sensitive to externally applied pressure and can survive even below T_o. We note that many choices of hierarchy other than the Cayley tree could also be possible.

The notion of a connected hierarchy of domain wall separations ranging from macroscopic to atomic length scales allows for a possible mechanism of shape memory in which macroscopic stress variations can be fed down to atomic scales and then recovered in an appropriate pressure/temperature cycle. The hierarchy of length scales (e.g. $\AA \rightarrow cm$) provides a hierarchy of time scales (e.g. nanoseconds $\rightarrow$ minutes) and hence the possibility of non-exponential decay [12]. For instance, if energy barriers go up linearly with hierarchical generations $E_n \sim nE_1$, then decays are power law, $\sim t^{-T/E_1}$. This implies that low temperatures (martensite) correspond to slower processes while high temperatures (austenite) correspond to faster processes. Again, this time behavior is essential for the shape memory cycle.

The above ideas are embodied in the following (dimensionless) elastic model Hamiltonian:

$$H = H_{bulk} + H_{grad} + H_{\alpha} + H_{twin}, \tag{1}$$

$$H_{bulk} = \sum_i \left[(\tau - 1)\epsilon_i^2 + \epsilon_i^2(\epsilon_i^2 - 1)^2\right] - \sum_i P_i\epsilon_i, \qquad \tau = \frac{T - T_c}{T_o - T_c}. \tag{2}$$

$$H_{grad} = \frac{a}{4}\sum_i \left[(\nabla_x\epsilon_i)^2 + (\nabla_y\epsilon_i)^2\right] + \frac{b}{8}\sum_i \left[(\nabla_x^2\epsilon_i)^2 + (\nabla_y^2\epsilon_i)^2\right]. \tag{3}$$

$$H_\alpha = -\frac{\alpha}{8}\sum_i (\nabla_x^2 \epsilon_i)(\nabla_y^2 \epsilon_i). \tag{4}$$

$$H_{twin} = \nu \sum_{i \neq j} \frac{\epsilon_i \epsilon_j}{|r_i - r_j|}. \tag{5}$$

Here ϵ_i are dimensionless, scaled local shear strains defined on the sites of a 2D square lattice; P_i and τ are dimensionless stress and scaled temperature in the ϕ^6 model, respectively. T_c denotes the temperature at which the shear modulus would soften completely, i.e. the elastic constants would satisfy $C_{11} = C_{12}$. Of the three elastic gradient coefficients (a, b, α), b and α are possibly modified by compositional fluctuations, and are necessarily positive. The gradient terms (H_{grad} and H_α) are evaluated using discréte derivatives on the lattice. For $P = 0, H_{bulk}$ has three minima for $0 < \tau < \frac{4}{3}$, one minimum at $\epsilon = 0$ (pure austenite) for $\tau > \frac{4}{3}$, and two side minima (two pure martensitic variants) for $\tau < 0$. The range for stable tweed is $1 < \tau < \frac{4}{3}$. There are three degenerate minima at $\tau = 1$. H_{twin} represents the habit plane-mediated long range elastic interaction (of strength ν) which stabilizes twins below T_o [4]. $|r_i - r_j|$ denotes the distance between sites i and j on the square lattice.

III. STATICS

To obtain analytic estimates for the energy and equilibrium size (L^*, W^*) of tweed plus hierarchy (see Fig. 2c below) at a given temperature and pressure (stress) we consider a "skeleton" approximation in which (i) only three possible values of strain (ϵ_i), namely ϵ_0, ϵ_+, and ϵ_- corresponding to the austenite and two variants of martensite, respectively, are considered; (ii) domain wall (twin boundary) between ϵ_+, and ϵ_- or habit plane between ϵ_0 and ϵ_+ (or ϵ_-) are atomically sharp; (iii) a Cayley tree type hierarchy (i.e. regions of alternating ϵ_+ and ϵ_- strain distribution increasing in size progressively away from the habit plane) is assumed to give as many domain walls and intersections as possible. The tweed pattern corresponds to a checkerboard strain distribution of ϵ_+ and ϵ_-.

The gradient terms contribute to the total energy across the interface (habit plane or twin boundary) and near the corners. In particular, for creating an interface H_{grad} costs energy but H_α has no effect. In contrast, H_α favors intersections (corners) but H_{grad} does not contribute to the energy of corners. Thus, the system strikes a compromise by creating tweed in most of the bulk and hierarchical (branched) domain walls near the habit plane. Therefore, the total energy is $E^{total} = E^{tweed} + E^{hier}$, where

$$E^{tweed} = AL^2 + 4(a+b)\psi_+ L + 2(a+b)\phi n_D L - 2\alpha\phi n_D(1+n_D),$$

$$E^{hier} = -4n_D\Big(2\alpha\phi - (a+b)(\psi_+ + \psi_- + (4+n_0)\phi)\Big)\left(\frac{L}{n_D+1} - 1\right),$$

$$A = \frac{1}{2}\sum_{\mu=\pm} E_{bulk}(\epsilon_\mu) - E_{bulk}(\epsilon_0), \quad E_{bulk}(\epsilon) = (\tau-1)\epsilon^2 + \epsilon^2(\epsilon^2-1)^2 - P\epsilon,$$

$$n_D = \frac{L}{Wa_o} - 1, \quad n_o = ln\frac{W+1}{2}; \quad \phi = \left(\frac{\epsilon_+ - \epsilon_-}{2}\right)^2, \quad \psi_\pm = \left(\frac{\epsilon_\pm - \epsilon_0}{2}\right)^2.$$

In the skeletal model the total number of domain walls (with separation Wa_o) is n_D and the number of generations in the hierarchy equals n_o, where a_o is the minimum separation between two domain walls at the habit plane in units of lattice constant. The parameter range for stable tweed is determined from

$$b > (a+b)^3 > \alpha > a+b > 1.$$

This condition holds for $a < 0$ and $b > 0$ (and α must be positive). For $P = 0$, $\phi = 1$ and $\psi_\pm = \frac{1}{4}$.

Minimization of E^{total} with respect to L (or equivalently W) for parameters satisfying the above condition indeed leads to a stable tweed with equilibrium size (L^*, W^*). The variation of equilibrium tweed width W^* as a function of temperature is shown in Fig. 1 for representative parameters. Note that in the absence of external (or internal) stress tweed coarsens upon cooling toward T_o (see Fig. 1). The region of equilibrium tweed size $L^* = W^* a_o(n_D + 1)$ increases proportional to the equilibrium tweed modulation width W^*. Below $\sim T_o$ there is no tweed and above a critical temperature (T^{upper}, which depends on the coefficients of the gradient terms: a, b, α) tweed becomes unstable to the formation of austenite. These results are qualitatively consistent with experimental observations [1,2]. In the presence of external stress we find that tweed can exist even below T_o. This is essential for realizing the shape memory cycle.

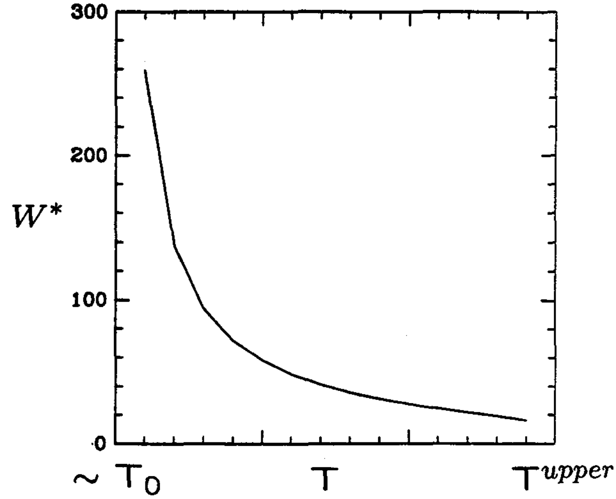

FIG. 1. Equilibrium tweed width as a function of temperature for representative parameters.

IV. DYNAMICS

We consider strain variables ϵ_i on an NxN 2D square lattice (N=96) of atomic (unit) scale. The simulations are based on molecular dynamics with the above static tweed Hamiltonian as a potential for the deterministic force term. The equation for the evolution of the strain in the system, after quenching, is given by

$$\frac{\partial \epsilon_i}{\partial t} + \frac{1}{\eta_0}\frac{\partial^2 \epsilon_i}{\partial t^2} = -\phi_0 \frac{\delta H}{\delta \epsilon_i} + \sigma_i, \tag{6}$$

where η_0 is the dimensionless viscosity, ϕ_0 is the relative strength of elastic energy to thermal energy, and σ_i represents noise of various forms, e.g. Langevin white noise. The latter satisfies the fluctuation-dissipation relationship:

$$< \sigma_i(t)\sigma_j(t') >= 2\frac{T}{T_0}\delta_{ij}\delta(t-t') \ , \tag{7}$$

where T and T_0 are the temperature and the martensitic transition termperature of the system, respectively. For the results shown here the second term on the left-hand-side of equation (6) and the noise term are omitted.

Preliminary results are shown in Fig. 2 for representative parameter values. Modulated twins (in the presence of external stress) for $T < T_o$ are depicted in Fig. 2a. The white and black regions correspond to the two martensitic variants. The long range interaction term H_{twin} was appropriately treated with a cut-off. For $\sim T_o < T < T^{upper}$ a typical tweed structure with varying length scales is shown in Fig. 2b. A preliminary pattern for tweed with hierarchy is depicted in Fig. 2c, where the interior (bulk) consists of coarse tweed and the periphery comprises branched domain walls becoming finer as the habit plane is approached.

Having shown the formation of tweed and hierarchy, we are now in a position to address the question of shape memory. A particular shape is given to the alloy at high temperature (above the transition temperature T_o in the austenite phase). The alloy is then cooled below T_o (in the twinned martensite phase) and the shape is randomly changed by applying external stress. When the alloy is reheated above T_o the alloy recovers its original shape.

By refining our simulations we expect to be able to demonstrate that (i) an external spatially varying stress ("good" message) induces corresponding spatial domain wall variations in the tweed (WRITE process). (ii) This spatial tweed variation feeds down at $T > T_o$ into the connected hierarchical blocks that terminate the domain walls. Since the splitting is of the Cayley tree type, this implies a feeding of information down to atomic scale (RECORD process). (iii)

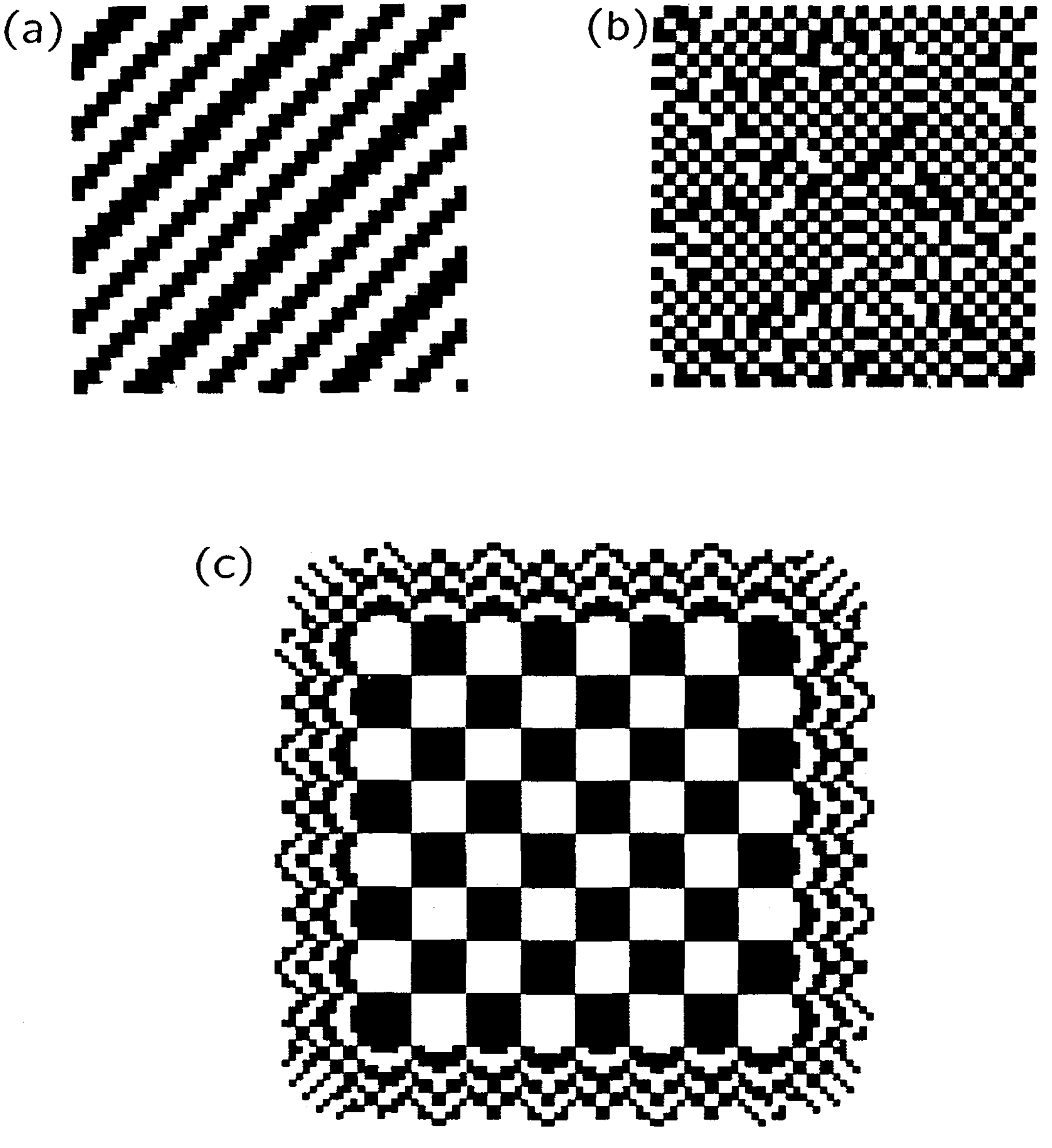

FIG. 2. (a) Modulated twin bands, (b) tweed, and (c) hierarchical tweed pattern for representative parameters.

On cooling $T < T_o$ a competing, e.g. random, spatially varying stress ("bad" message) induces tweed variations on the macroscopic scale (ERASE process). Since at low temperatures hierarchical structure variations are non-exponential (slow) [12] in time the good message remains recorded at lower levels. (iv) On warming above T_o the lower level hierarchies produce internal stress that drives a regeneration of the erased macroscopic pattern of the good message (RECALL process). In general, we expect that disorder as well as noise sources of the above and other forms will truncate the hierarchy below a certain level (generation), thus introducing "generational amnesia" below that level.

V. CONCLUSION

We have synthesized several ideas in the literature and a variety of properties specific to martensitic materials based on experimental observations and theoretical calculations to construct a phenomenological model that can satisfactorily describe (i) twins, (ii) tweed, and (iii) shape memory phenomena. Hierarchical twinning of domain walls is a novel and crucial feature of this model. In particular, the model contains two key ingredients, namely a cross-derivative gradient term that favors domain wall crossing, and the idea of hierarchical Cayley tree splitting of the domain walls from atomic scales at the habit plane to macroscopic scales inside the tweed. Specifically, tweed was obtained as a free energy minimum and its existence was demonstrated in simulations. We also suggested that hierarchically stabilized tweed microstructures can possibly lead to shape memory. Finally, we note that the above discussion and results do not apply to all martensitic materials but to a limited class of materials.

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[1] L.E. Tanner, A.R. Pelton, and R. Gronsky, J. de Phys. Suppl. 12 **43**, C4 (1982); P.C. Clapp, J. Rifkin, J. Kenyon, L.E. Tanner, Metall. Trans. A. **19**, 783 (1988); R. Oshima, M. Sugiyama, and F.E. Fujita, Metall. Trans. A **19**, 803 (1988).
[2] M. Sugiyama, Ph. D. Thesis, Osaka University, 1985.
[3] W.S. Wechsler, D.S. Lieberman, and T.A. Read, Trans. AIME **197**, 1503 (1953).
[4] G.R. Barsch, B. Horovitz, and J.A. Krumhansl, Phys. Rev. Lett. **59**, 1251 (1987); B. Horovitz, G.R. Barsch, and J.A. Krumhansl, Phys. Rev. B **43**, 1021 (1991).
[5] S. Semenovskaya and A.G. Khachaturyan, Phys. Rev. Lett. **67**, 2223 (1991); Physica D **66**, 205 (1993); S. Semenovskaya, Y. Zhu, M. Suenaga, and A.G. Khachaturyan, Phys. Rev. B **47**, 12182 (1993).
[6] See e.g. *Proc. International Conference on Martensitic Transformations* (ICOMAT-92), eds. C.M. Wayman and J. Perkins (Monterey Institute of Advanced Studies, California, 1993).
[7] G.R. Barsch and J.A. Krumhansl, Phys. Rev. Lett. **53**, 1069 (1984); Metallurg. Trans. A **19**, 761 (1988).
[8] S. Kartha, T. Kastàn, J.A. Krumhansl, and J.P. Sethna, Phys. Rev. Lett. **67**, 3630 (1991); J.P. Sethna, S. Kartha, T. Kastàn, and J.A. Krumhansl, Phys. Scripta **T42**, 214 (1992).
[9] S. R. Shenoy, A. Saxena, A. R. Bishop, and P. S. Lomdahl, Bull. Am. Phys. Soc. **39**, 909 (1994).
[10] P.C. Clapp, Physica D **66**, 26 (1993); in Phase Transformations '87, ed. G. W. Lorimer, Inst. of Metals, London (1988), p. 391.
[11] R.V. Kohn and S. Müller, Phil. Mag. A **66**, 697 (1992).
[12] B.A. Huberman and M. Kerszberg, J. Phys. A: Math Gen. **18** L331 (1985).