Theory of ductility: From brittle to superplastic behavior of polycrystals

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The plastic flow of a polycrystal is calculated assuming that no sliding does occur if the in-plane components of the shear stress acting on the common grain boundary of two grains are below a threshold stress τ_c. Otherwise the grains slide with relative velocity proportional to the in-plane shear stress. The trace of the resulting strain rate tensor does not vanish for finite threshold stress, indicating that the grains of the material are increasingly compressed as the sample is being stretched. The internal pressure helps deformation, and under some precise physical circumstances the material becomes mechanically unstable. The effect is very sensitive to the material constants and can explain extreme brittleness or large ductility. The approach can be extended to amorphous materials.

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I. INTRODUCTION

Brittle solids fracture almost immediately after the proportional limit of the strain-stress curve is reached, and the largest strain rarely exceeds 1%. Close to this point the stress has a peak, and the slope of the curve jumps to a large negative value, which determines a highly unstable mechanical condition. In opposition to neckless brittle fracture, ductile failure takes place after some homogeneous plastic deformation, characterized by work hardening of the material, followed by the generation of surface instabilities that lead to the neck formation that precipitates fracture. Plastic strains beyond 20% are very seldom, which is not a trivial fact. Superplastic materials may be considered as an intermediate situation, in which the flow stress is almost independent of strain, which is a necessary condition for an almost stationary flow regime.

For more than 80 years, the research on brittle and ductile behavior of solids has assumed Griffith's hypothesis that brittle materials have microscopic cracks that lower their overall strength because concentrate stress when loaded.[1] To prove his assertion, Griffith prepared a supposedly crack-free glass rod, which resisted up to 6300 MPa in bending, whereas the normal strength of the material was only 183 MPa. However, the much lower usual strength was spontaneously recovered within a few hours, indicating that the presence of weakening defects is a natural condition for thermodynamical equilibrium. Griffith's pioneer work was subsequently modified by Irwin[2–4] and Orowan[5–7] to extend it to ductile materials.

Present day research in the field strongly relies on computer simulations of cracks in crystals, to elucidate their stress driven time evolution.[8,9] According to current models, a crack may propagate conserving its atomically sharp edge, leading to brittle fracture. Alternatively, the material in front of the crack tip may react, nucleating dislocations that rapidly propagate away from the crack, readily damping crack propagation, and leading to ductile behavior.[10–15] However, crack evolution has proven to be complex, and simulations demand too large computer capacity. The advent of practical conclusions from these efforts, of use in technical grounds, seems to be far away yet.

An entirely different approach to the fracture of solids is put forward in what follows, alternate but not necessarily contradictory to Griffith's hypothesis, because different materials may behave differently. Following Orowan, fracture is not a single physical phenomenon; there are several essentially different processes that may lead to the disintegration of a body by the action of mechanical forces. The ideas presented below can be applied to both amorphous and polycrystalline solids. However, for the sake of brevity, the scope is restricted to the latter.

It is shown here that even an ideal fine-grained polycrystalline material, free of voids and cracks, whose grains are prone to slide, readily accommodating each other's shapes, should fail after a finite plastic strain. The reason is an elementary condition that has been omitted in previous studies: whatever the mechanisms for stress-dependent grain boundary sliding and grain shape accommodation may be, they must be consistent with density conservation to produce a steady flow. However, it is shown in Sec. II that if the local in-plane shear stress causing grain sliding has a finite threshold, below which no sliding does occur, density is not conserved in the overall plastic flow. The grains are increasingly compressed as the sample is being stretched, and hence grain sliding can only proceed at the expenses of elastic volume variations of the crystallites. Section III shows how the consequent cumulative internal pressure helps deformation and leads to mechanical instability at a critical strain. The material may undergo either brittle or ductile fracture, depending on the precise physical circumstances.

II. DENSITY CHANGES IN THE PLASTIC DEFORMATION OF A POLYCRYSTAL

Consider the plastic deformation of the hypothetical ideal polycrystal referred to in the last paragraph of the preceding section. Attention is put on bulk matter, far from surfaces, and the grains are assumed equiaxed and oriented in an isotropic manner. The process involves both grain boundary sliding and efficient grain shape accomodation to preserve the full contact between adjacent crystallites. It is assumed that grains readily adapt their shapes by slip or twinning at the triple junctions, hence grain boundary sliding is the rate-limiting process at steady flow. It is assumed also that the relative velocity of two adjacent sliding grains is proportional to the in-plane components of the shear stress acting in the shared grain boundary plane.

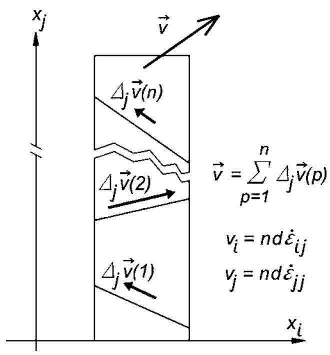

FIG. 1. A long narrow column along the j coordinate axis of the main (xyz) frame, cutting n grains of mean size d. The relative velocity $\boldsymbol{v}$ between the grains $p=0$ and $p=n$ determines the components $\dot{\varepsilon}_{ij}$ of the strain rate tensor.

Defining a local frame of reference $(x'y'z')$ whose $x'y'$ plane is in the common grain boundary plane of two adjacent grains, the components of the relative velocity between the grains is expressed as

$$\Delta v_{i'} = \begin{cases} \mathcal{Q}\sigma_{i'z'}, & \sqrt{\sigma_{x'z'}^2 + \sigma_{y'z'}^2} > \tau_c, \\ 0, & \sqrt{\sigma_{x'z'}^2 + \sigma_{y'z'}^2} \le \tau_c, \end{cases} \quad i' = x', y', \tag{1}$$

and always

$$\Delta v_{z'} = 0, \tag{2}$$

because the grain boundary does not displace along the normal coordinate z'. In Eq. (1) $\sigma_{i'j'}$ denotes the components of the stress tensor in the $(x'y'z')$ frame, τ_c is the critical shear stress for grain boundary sliding, and $\mathcal{Q}$ is a coefficient which will be discussed later.

The axes of the main frame of reference (xyz) will be along the principal directions of the stress tensor. Hence, calling σ_x, σ_y, and σ_z the principal stresses, the stress components in the rotated $(x'y'z')$ frame are given by

$$(\sigma_{i'j'}) = R(\theta,\phi)\begin{pmatrix} \sigma_x & 0 & 0 \\ 0 & \sigma_y & 0 \\ 0 & 0 & \sigma_z \end{pmatrix} R^T(\theta,\phi), \tag{3}$$

where

$$R(\theta,\phi) = \begin{pmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi\cos\theta & \cos\phi\cos\theta & \sin\theta \\ \sin\phi\sin\theta & -\cos\phi\sin\theta & \cos\theta \end{pmatrix}. \tag{4}$$

The rotation matrix R is such that the rotated x' axis remains in the xy plane, forming a Euler angle ϕ with the x axis, and the other Euler angle θ is the angle between the rotated z' and the old z axes. Performing (3),

$$\begin{aligned} \sigma_{x'z'} &= (\sigma_x - \sigma_y)\sin\phi\cos\phi\sin\theta, \\ \sigma_{y'z'} &= -(\sigma_x \sin^2\phi + \sigma_y\cos^2\phi - \sigma_z)\sin\theta\cos\theta. \end{aligned} \tag{5}$$

On the other hand, Fig. 1 shows the relation between the relative velocities $\Delta\boldsymbol{v}$ of adjacent grains, projected on the principal axes, and the strain rate tensor $\dot{\varepsilon}_{ij}$. If the boundary planes are oriented at random, one readily realizes that the sum appearing in Fig. 1 can be expressed as the average

$$\dot{\varepsilon}_{ij} = \frac{1}{d}\langle \Delta v_i \rangle_j, \quad i,j = x,y,z, \tag{6}$$

where the symbol $\langle\rangle_j$ means average over all orientations of the planes whose normal vectors have positive j component. The latter restriction ensures that Δv_i will represent the velocity of a grain relative to the previous one, along a column extending towards the positive direction of the j axis of the principal frame.

Equations (1), (2), and (5) determine the components of the relative velocity of two grains in the corresponding $(x'y'z')$ frame of their shared boundary plane. One can express them in the unique principal frame (xyz) by making the inverse transformation

$$\begin{pmatrix} \Delta v_x \\ \Delta v_y \\ \Delta v_z \end{pmatrix} = \mathcal{Q} R^T(\theta,\phi) \begin{pmatrix} \sigma_{x'z'} \\ \sigma_{y'z'} \\ 0 \end{pmatrix}, \tag{7}$$

where $\mathcal{Q}$ is assumed to depend on the stress components at most through the trace $\sigma_x+\sigma_y+\sigma_z$, which is not affected by the rotation. Explicitly,

$$\Delta\boldsymbol{v} = \mathcal{Q}\begin{pmatrix} (\sigma_x-\sigma_y)\sin\phi\cos^2\phi\sin\theta + (\sigma_x\sin^2\phi + \sigma_y\cos^2\phi - \sigma_z)\sin\phi\sin\theta\cos^2\theta \\ (\sigma_x-\sigma_y)\sin^2\phi\cos\phi\sin\theta - (\sigma_x\sin^2\phi + \sigma_y\cos^2\phi - \sigma_z)\cos\phi\sin\theta\cos^2\theta \\ -(\sigma_x\sin^2\phi + \sigma_y\cos^2\phi - \sigma_z)\sin^2\theta\cos\theta \end{pmatrix}. \tag{8}$$

Assume now that the material is subjected to an uniaxial external stress σ_z. Far from the surfaces of the sample, the system has cylindrical symmetry and hence $\sigma_x=\sigma_y$, which will be assumed not to vanish for the sake of generality. From Eqs. (5), $\sigma_{x'z'}=0$ for any boundary plane and $\sigma_{y'z'}=(\sigma_z-\sigma_x)\sin\theta\cos\theta$ accounts for the whole shear stress. This is a simple geometrical consequence of the choice of the rotated frame $(x'y'z')$, whose x' direction is always in the xy plane of the main frame (xyz). The grain boundary will slide only if $|\sigma_{y'z'}| > \tau_c$. Therefore, grain boundary sliding demands that

$$|(\sigma_z - \sigma_x)\sin\theta\cos\theta| > \tau_c \quad (\sigma_x = \sigma_y), \tag{9}$$

which determines a critical angle θ_c, given by

$$\sin(2\theta_c) = \frac{2\tau_c}{|\sigma_z - \sigma_x|} \quad (\sigma_x = \sigma_y). \tag{10}$$

Sliding can occur only for $|\sin(2\theta)| > \sin(2\theta_c)$.

Replacing $\sigma_x = \sigma_y$, Eq. (8) reduces to

$$\Delta \boldsymbol{v} = \mathcal{Q}(\sigma_z - \sigma_x)\begin{pmatrix} -\sin\phi\cos^2\theta\sin\theta \\ \cos\phi\cos^2\theta\sin\theta \\ \sin^2\theta\cos\theta \end{pmatrix}, \tag{11}$$

from which can be calculated the averages over solid angles 2π around the principal axes, less the regions determined by $|\sin(2\theta)| > \sin(2\theta_c)$:

$$\langle \Delta v_z \rangle_z = \frac{1}{2\pi}\int_0^{2\pi} d\phi \int_{\theta_c}^{\pi/2-\theta_c} d\theta \sin\theta \Delta v_z, \tag{12}$$

$$\langle \Delta v_x \rangle_x = \frac{1}{2\pi}\int_0^{\pi} d\phi \left(\int_{\theta_c}^{\pi/2-\theta_c} d\theta + \int_{\pi/2+\theta_c}^{\pi-\theta_c} d\theta\right)\sin\theta \Delta v_x, \tag{13}$$

$$\langle \Delta v_y \rangle_y = \frac{1}{2\pi}\int_{\pi/2}^{3\pi/2} d\phi \left(\int_{\theta_c}^{\pi/2-\theta_c} d\theta + \int_{\pi/2+\theta_c}^{\pi-\theta_c} d\theta\right)\sin\theta \Delta v_y. \tag{14}$$

The off-diagonal terms vanish because of the parity of the subintegral functions.

Recalling (6), Eqs. (11)–(14) give

$$\dot{\varepsilon}_{zz} = \frac{\mathcal{Q}}{4d}(\sigma_z - \sigma_x)\cos(2\theta_c), \tag{15}$$

which in terms of the threshold stress τ_c reads

$$\dot{\varepsilon}_{zz} = \frac{\mathcal{Q}}{4d}\sqrt{(\sigma_z - \sigma_x)^2 - 4\tau_c^2}, \tag{16}$$

and

$$\dot{\varepsilon}_{xx} = \dot{\varepsilon}_{yy} = -\frac{\mathcal{Q}}{8d}(\sigma_z - \sigma_x)\left(1 - \frac{4\theta_c}{\pi} + \frac{\sin(4\theta_c)}{\pi}\right). \tag{17}$$

One can easily realize from these equations that the dilation rate $\dot{V}/V = \dot{\varepsilon}_{xx} + \dot{\varepsilon}_{yy} + \dot{\varepsilon}_{zz}$,

$$\frac{\dot{V}}{V} = -\frac{\mathcal{Q}}{4d}(\sigma_z - \sigma_x)\left(1 - \cos(2\theta_c) - \frac{4\theta_c}{\pi} + \frac{\sin(4\theta_c)}{\pi}\right), \tag{18}$$

where V stands for the volume of the sample, vanishes only when the threshold stress $\tau_c = 0$. As the dilation rate is negative for $\sigma_z - \sigma_x > 0$, stretching the sample involves a compression of the grains, which can only be elastic. The transversal stresses σ_x and σ_y take in general finite values, even when they vanish at start; therefore, the single-crystal elastic compressibility and strength will determine how much the polycrystal could be elongated.

The dilation rate given by Eq. (18) can be easily understood in qualitative terms by a simple geometric argument. No matter how strong the external forces may be, shear stresses vanish in the planes normal to the principal directions. Thus, by continuity, there is a cone around the z axis, subtending an angle $2\theta_c$, in which shear stresses are smaller than τ_c. Sliding is forbidden for any grain boundary whose normal is inside this solid angle. In a pictorial way, no sliding can occur within the two *polar circles* of the sphere of unit vectors normal to the grain boundary planes.

On the other hand, because of the cylindrical symmetry, any direction in the xy plane is a principal direction. Hence, shear stresses vanish in any plane whose normal is in the xy plane. Reasoning the same way as before, one concludes that sliding is prohibited also in the *tropical region* of the sphere of unit normal vectors.

As the tropical region subtends the same angle $2\theta_c$, it has larger area than the polar circles. Therefore, $\tau_c \neq 0$ determines that grain displacements in the z direction, or close to it, be less favored than those occurring in directions near the xy plane. If no dilation takes place when $\tau_c = 0$, some volume change should occur for $\tau_c \neq 0$.

III. INTERNAL PRESSURE BUILDUP AND CRITICAL STRAIN

In what follows we will examine the case of the uniaxial plastic strain of a bulk sample along the z axis at a constant strain rate $\dot{\varepsilon} \equiv \dot{\varepsilon}_{zz}$. The only externally applied stress is $\sigma \equiv \sigma_z$. Just for taking advantage of the better insight that provides explicit analytical expressions, let us restrict ourselves to situations for which $\sin(2\theta_c) \ll 1$. The exact equation for the dilation rate then reduces to

$$\frac{\dot{V}}{V} = -\frac{\tau_c^2}{2d(\sigma_z - \sigma_x)}\mathcal{Q} \quad (\sigma_z - \sigma_x \gg \tau_c). \tag{19}$$

Denoting

$$p = -(\sigma_x + \sigma_y + \sigma_z)/3 \tag{20}$$

the internal pressure, recalling Hooke's law

$$\frac{\Delta V}{V} = -\frac{p}{B}, \tag{21}$$

where B is the bulk modulus, and Eq. (16), and combining them with Eq. (19) and the identity

$$\frac{1}{V}\frac{dV}{d\varepsilon} = \frac{\dot{V}}{V}\frac{1}{\dot{\varepsilon}}, \tag{22}$$

one finally obtains that

$$\frac{dp}{d\varepsilon} = \frac{B\tau_c^2\mathcal{Q}}{2d\dot{\varepsilon}\sqrt{(4d\dot{\varepsilon}/\mathcal{Q})^2 + 4\tau_c^2}}. \tag{23}$$

In the new notation, $\sigma_z - \sigma_x = 3(\sigma + p)/2$. Notice that ε denotes purely plastic strain.

As $\mathcal{Q} = \mathcal{Q}(p)$, Eq. (23) is a first-order differential equation for the internal pressure buildup $p(\varepsilon)$ upon deformation. If the material has no residual stresses at start, then $\sigma_x = \sigma_y = 0$ for $\varepsilon = 0$ and the initial condition for (23) is $p(0) = -\sigma_0/3$, where σ_0 is the flow stress at $\varepsilon = 0$ (σ_0 is in practice the yield stress, or close to it).

If $\mathcal{Q}$ were a constant, the solution of Eq. (23) would be immediate. Integrating and combining with Eq. (16) one would conclude that the material softens linearly with deformation according to

$$\sigma = \sigma_0 - \frac{2B\tau_c^2}{\sigma_0\sqrt{\sigma_0^2 - 4\tau_c^2}}\varepsilon \quad (\mathcal{Q} = \text{const}), \tag{24}$$

where $\sigma_0 = \sqrt{(4d\dot{\varepsilon}/\mathcal{Q})^2 + 4\tau_c^2}$.

Replacing in Eq. (24) $B = 10^5$ MPa, $\tau_c = 1 - 10$ MPa, and $\sigma_0 = 27$ MPa, as typical values, one obtains that the expression is consistent with a brittle material that may resist 0.1% plastic elongation prior to fracture, and a more ductile material that could be elongated to a 10% true strain. These figures follow from the very extreme condition that fracture takes place when σ falls to zero.

However, it is expected that $\mathcal{Q}$ should be stress and temperature dependent. Assuming the mechanism for grain boundary sliding put forward in Refs. 16 and 17, one has that

$$\frac{\mathcal{Q}}{4d} = C_0 \frac{\Omega^*}{k_B T} \exp\left(-\frac{\epsilon_0 + \Omega^* p}{k_B T}\right), \tag{25}$$

where C_0 is a constant depending only on the grain size, grain boundary thickness, and the preexponential factor of the diffusion coefficient for vacancies, Ω^* is an activation volume, k_B is the Boltzmann constant, T is the temperature, and ϵ_0 is the energy necessary for the grain boundary to release a vacancy. Replacing in Eq. (23) and solving the resulting differential equation, it is obtained that

$$\varepsilon = \frac{k_B T}{B\Omega^*}[f(\chi) - f(\chi_0)], \tag{26}$$

where the auxiliary functions f and χ are defined by $f(\chi) = \chi\sqrt{\chi^2+1} + \ln(\chi + \sqrt{\chi^2+1})$, and

$$\chi = \frac{k_B T \dot{\varepsilon}}{2C_0\Omega^*\tau_c} \exp\left(\frac{\epsilon_0 + \Omega^* p}{k_B T}\right). \tag{27}$$

The constant χ_0 follows from placing $-\sigma_0/3$ instead of p in Eq. (27). The yield stress σ_0 at $\varepsilon = 0$ is determined by

$$\dot{\varepsilon} = C_0 \frac{\Omega^*}{k_B T}\sqrt{\sigma_0^2 - 4\tau_c^2} \exp\left(-\frac{\epsilon_0 - \Omega^*\sigma_0/3}{k_B T}\right). \tag{28}$$

Hence one can obtain the stress $\sigma(\varepsilon; T, \dot{\varepsilon})$ for uniaxial plastic deformation at constant strain rate $\dot{\varepsilon}$ solving (26) for χ, isolating p from (27), and then replacing in

$$\sigma = \frac{4\tau_c}{3}\sqrt{\chi^2+1} - p \quad \left(\sqrt{\chi^2+1} \geqslant \tfrac{1}{2}\right). \tag{29}$$

The condition written with Eq. (29) ensures that the approximation (19) remains valid. Notice that in the new notation $\sigma_z - \sigma_x = 3(\sigma + p)/2$.

To illustrate how the function $\sigma(\varepsilon; T, \dot{\varepsilon})$ obtained by this procedure can explain brittle and ductile behavior, it was applied to Ti-6Al-4V, a superplastic alloy very popular in airplane design. The alloy was chosen because the constitutive parameters ϵ_0, Ω^*, and C_0, appearing in Eq. (25), are known with good precision.[16] The only unknown constant is the threshold stress τ_c, but no attempt to determine it was done because the present purposes are only illustrative. The temperature $T = 1183$(K) was selected because it has particular interest, as it optimizes the superplastic properties of the material. The curves in Fig. 2 represent Eq. (29), with χ and p given by Eqs. (26)–(28). To have a feeling of how well they reproduce real facts, the reader may examine the data in Fig. 5 of Ref. 18.

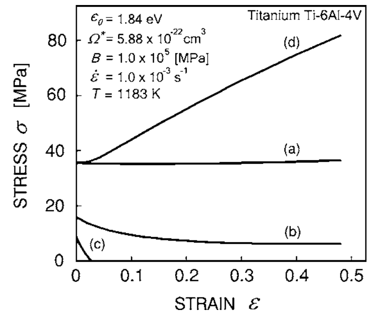

FIG. 2. Plastic stress-strain curves for Ti-6Al-4V, as given by Eq. (29). The constitutive constants are essentially those of Ref. 16 (a), with variations to produce work softening (b), brittle fracture (c), and work hardening (d).

Curves (a) and (d) were obtained with ϵ_0, Ω^*, and C_0 taken from Ref. 16, but with $\tau_c = 0.5$ MPa in (a) and $\tau_c = 2.0$ MPa in (d). The curves show that a moderately high value of τ_c can induce work hardening, a characteristic feature of ductile materials.

Curves (b) and (c) assume $\tau_c = 0.5$ MPa, as curve (a), but the constitutive parameter C_0 was increased from 3.52×10^4 s^{-1} (a),[16] to 1.0×10^5 s^{-1} (b), and 2.0×10^5 s^{-1} (c). As C_0 varies with the grain size d as d^{-3}, the three curves correspond to $d = 2.28$ μm,[16] $d = 1.61$ μm, and $d = 1.28$ μm. Curve (b) exhibits work softening and (c) brittle fracture for $\varepsilon = 0.028$.

IV. NECKING AND DUCTILE FRACTURE

Ductile fracture occurs with the help of p. Recall that the internal stress along the tensile axis is not σ alone, but

$$\sigma_{\text{eff}} \equiv \sigma_z - \sigma_x = \tfrac{3}{2}(\sigma + p). \tag{30}$$

At $\varepsilon = 0$ one has that $\sigma = \sigma_0$, and $p(0) = -\sigma_0/3$ is negative, giving $\sigma_{\text{eff}} = \sigma$. However, for large enough ε the pressure p becomes positive and contributes to enhance the effective tensile stress $\sigma_{\text{eff}} \equiv 3(\sigma + p)/2$. On the other hand, in the latter situation,

$$\sigma_x = \sigma_y = -\tfrac{1}{2}(\sigma + 3p) \tag{31}$$

is negative and constitutes a bidimensional hydrostatic pressure applied in the plane normal to the tensile axis. Hence, failure occurs by the concurrent action of a tensile stress along the z axis with an isotropic compression stress in the xy plane, both being of comparable magnitudes. In this picture, necking becomes a very natural feature of ductile fracture.

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[1] A. A. Griffith, Philos. Trans. R. Soc. London, Ser. A **221**, 163 (1920).

[2] G. R. Irwin, in *Fracturing of Metals* (American Society of Metals, Cleveland, OH, 1948), p. 147.

[3] G. R. Irwin, in *Proceedings of the 2nd Sagamore Conf. Ordnance Materials*, Vol. II (Syracuse U. P., Syracuse, NY, 1956), p. 289.

[4] G. R. Irwin, in *Encyclopedia of Physics, Vol. VI. Elasticity and Plasticity*, p. 551, edited by S. Flüge (Springer–Verlag, Berlin, 1958).

[5] E. Orowan, Trans. Inst. Shipbuilders Scotland **89**, 165 (1945).

[6] E. Orowan, Rep. Prog. Phys. **12**, 185 (1948).

[7] E. Orowan, Welding J. Res. Sup. **34**, 157 (1955).

[8] H. Henry and H. Levine, Phys. Rev. Lett. **93**, 105504 (2004).

[9] G. G. Batrouni and A. Hansen, Phys. Rev. Lett. **80**, 325 (1998).

[10] D. J. Green, R. Tandonand, and V. M. Sglavo, Science **283**, 1295 (1999).

[11] J. R. Rice and R. Thompson, Philos. Mag. **29**, 73 (1974).

[12] M. Khantha, D. P. Pope, and V. Vitek, Phys. Rev. Lett. **73**, 684 (1994).

[13] P. B. Hirsch, S. G. Roberts, and J. Samuels, Proc. R. Soc. London, Ser. A **421**, 25 (1989).

[14] A. Hartmaier and P. Gumbsch, Phys. Status Solidi B **202**, R1 (1997).

[15] P. Gumbsch, J. Riedle, A. Hartmaier, and H. F. Fischmeister, Science **282**, 1293 (1998).

[16] M. Lagos, Phys. Rev. B **71**, 224117 (2005).

[17] M. Lagos, Phys. Rev. Lett. **85**, 2332 (2000).

[18] M. T. Cope, D. R. Evetts, and N. Ridley, J. Mater. Sci. **21**, 4003 (1986).