

## Thermodynamics of dislocations and shock compression of solids

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A thermodynamic theory of dislocations is developed to provide a unified account of adiabatic shear and melting observed in metals and minerals under shock-wave compression. The theory contains two significant features. The first is the differentiation of irreversible energy changes from those of equilibrium energy functions. The second is the inclusion of dislocation dilatation. When applied to shock compression, it reveals a thermodynamic condition of instability based upon a principle of positive-entropy production for irreversible processes. This instability may be identified as adiabatic shearing or heterogeneous melting in the plane of maximum shear. The numerical results for selected materials from metals and minerals are in agreement with experimental observations, and show that the shear yielding becomes critical at about half the melting temperature and the dislocation density of about  $10^{15}/\text{m}^2$ .

### I. INTRODUCTION

The view presented in this paper is the result of our effort to synthesize three concepts into an articulated unity. They are (1) homogeneous and heterogeneous melting of solids under shock compression, (2) the dislocation theory of melting, and (3) thermodynamics of dislocations.

There is now a substantial amount of evidence that solids can melt during strong shock-wave loadings.<sup>1</sup> According to this review,<sup>1</sup> the homogeneous melting can be described by models based upon a nonequilibrium mixture of a solid and its melt in extended equilibrium states. Exceptions are found in quartz and other minerals, and their behavior is explained as heterogeneous melting caused by the localized loss of shear strength. Experimentally the latter is often identified by the appearance of intergrown diaplectic glass in recovered specimen<sup>2-5</sup> and observations of loss of shear strength under shock loading.<sup>6,7</sup> A similar catastrophic loss of shear strength is also known to occur in metals and polymers, and is discussed under the name of adiabatic shearing.<sup>8,9</sup>

The dislocation theory of melting considers a liquid as a solid densely packed with dislocations. Melting occurs spontaneously when the free energy of dislocations vanishes at a critical temperature.<sup>10-12</sup> The recent refinement<sup>11</sup> yields results which are comparable with those of computer simulation of melting.<sup>13</sup> A pleasing feature of the theory is that the basic element is the same dislocation that is often used for describing the mechanics of plastic deformation under shock loadings.<sup>14,15</sup> However, no immediate merging of the two theories has yet been accomplished.

There are many theories<sup>16-20</sup> that attempt to integrate dislocations into a thermodynamic formalism, but they are mostly concerned with their mechanical behaviors.<sup>21</sup> For instance, no attempt

has been made yet to clarify why the detailed calculations of thermodynamic parameters showed that such a theory might contain an incompatible anomaly.<sup>22</sup> There exists a need for the thermodynamic theory that accommodates both the thermal and mechanical properties of dislocations in dynamic irreversible flow, while providing a framework for melting at high temperatures. In addition, none of the above theories discusses dislocation dilatation<sup>23,24</sup> which plays an essential role in the dislocation theory of melting.<sup>11</sup> This may be attributed to the fact that the dislocation dilatation is considered to be a second-order effect at the density of, say,  $10^{13} \text{ m}^{-2}$  which is sufficiently large for plastic flow.<sup>15</sup> But locally the density can easily reach the magnitude of  $10^{16} \text{ m}^{-2}$  which induces not insignificant dilatation at high pressures.

Therefore, we have attempted to develop the thermodynamics of materials containing dislocations that can be extended for investigation of melting under shock loadings. Section II describes the theory, which is essentially a synthesis of work in Refs. 11 and 22. Section III discusses some thermodynamic features of the theory when applied to shock loadings. It contains a new thermodynamic criterion of instability which may be associated with heterogeneous melting or adiabatic shearing. Also it sheds some light on the phenomena of melting and shear instability.<sup>25</sup> Section IV illustrates some specific examples from minerals and metals.

### II. THERMODYNAMICS OF SOLIDS CONTAINING DISLOCATIONS

For simplicity we shall deal only with closed systems and assume that solids can be sufficiently represented by underlying elastic lattice strain  $\bar{\epsilon}_e$ , temperature  $T$ , and dislocation density  $\nu$ .

Then the thermodynamics of the solids can be built on two basic postulates. The first concerns the internal energy and the conservation of energy, and the second the definition of entropy. The extension of the theory for open systems and other defects may be handled as that for classical chemical systems.

First, we assume that there exists a function for the equilibrium internal energy of a solid  $E^*$  consisting of lattice and dislocation energies:

$$E^* = E_L(\bar{\epsilon}_e, T) + nE_d(\bar{\epsilon}_e, T), \quad (1)$$

where  $E^*$  is the internal energy per unit mass,  $E_L$  the lattice energy,  $n$  the fixed total length of dislocation per unit mass, and  $E_d$  the dislocation energy per unit length. We can consider a more complex expression for the dislocation energy than the above, but there is no experimental data that justifies such a complication at the moment.

The first law of thermodynamics for closed systems is

$$dE = dQ + dW, \quad (2)$$

where  $dQ$  and  $dW$  are the heat and work input, respectively, and  $dE$  the internal-energy change. But, since the dislocation-density change is mostly caused by irreversible plastic flow, the internal-energy change  $dE$  cannot be the exact differential of  $E^*$ . Hence, we shall assume that  $dE$  involving irreversible flow is given by a new relation,

$$dE = dE_L + n dE_d + E_d^p dn, \quad (3)$$

where  $E_d^p$  is a function of  $\bar{\epsilon}_e$ ,  $T$ ,  $n$ , etc., and is the irreversible internal energy associated with the change of dislocation density. Following Glansdorff and Prigogine,<sup>26</sup> Eq. (3) may be referred to as the excess internal-energy relation. The assumption emphasizes the difference between the change of an equilibrium energy function and that of an irreversible process involving nonequilibrium internal defects.

Second, we shall introduce another postulate to define local entropy. Here we find the assumption advanced by Duvall and Dandekar<sup>22</sup> most useful: "The elastically strained state imbedded in every deformed state is inherently reversible." To this, we add that elastic deformation does not change the dislocation density. Then following standard arguments in classical thermodynamics,<sup>27</sup> we can define local entropy  $S^*$  as follows,

$$dQ = dE^* - dW_e = T dS^*, \quad (4)$$

where  $dW_e$  is the reversible elastic work increment. Choosing matching measures of stress  $\bar{\sigma}$  and strain  $\bar{\epsilon}_e$ , we can define the work increment

as

$$dW_e = V_0 \bar{\sigma} \cdot d\bar{\epsilon}_e, \quad (5)$$

where  $V_0$  is a reference specific volume. Then, one finds from Eqs. (4) and (5)

$$\bar{\sigma} = \rho_0 (\partial E^* / \partial \bar{\epsilon}_e)_{S^*}, \quad (6)$$

$$T = (\partial E^* / \partial S^*)_{\bar{\epsilon}_e}, \quad (7)$$

where  $\rho_0 = 1/V_0$ . Now on combining Eqs. (2) and (4), we obtain the entropy change for general deformation including plastic flow:

$$T dS^* = dW_p - E_d^p dn + dQ, \quad (8)$$

where  $dW_p = dW - dW_e$  and the first and second terms on the right-hand side are the expressions for the irreversible entropy production due to plastic flow.

Once the entropy is established, we can introduce other thermodynamic functions. For instance, Helmholtz free energy  $F^*$  is given by

$$F^* = E^* - TS^* = E_L + nE_d - TS^*, \quad (9)$$

where  $n$  is again a constant. We can now define the excess free-energy relation analogous to Eq. (3).

$$dF = dE - d(TS^*) \quad (10)$$

$$\begin{aligned} &= E_d^p dn + dW_e - S^* dT \\ &= E_d^p dn + V_0 \bar{\sigma} \cdot d\bar{\epsilon}_e - S^* dT. \end{aligned} \quad (11)$$

Equation (11) yields a useful relation for determining  $E_d^p$ , i.e.,

$$E_d^p = (\partial F / \partial n)_{\bar{\epsilon}_e, T}. \quad (12)$$

This suggests that the energy associated with a dislocation-density change can be calculated by the proper identification of a partition function. One choice proposed by Ookawa<sup>28</sup> is the following:

$$F(\text{per atom}) = -kT \ln(z_n/z_0), \quad (13)$$

where  $z_n$  is the atomic partition function based on the ensemble containing  $n$  dislocations, and  $z_0$  the partition function for the ideal lattice. It is interesting to note that in this formalism the dislocation partition function need not be in equilibrium with that of the ideal lattice. This is consistent with the fact that dislocations are not equilibrium defects.<sup>23, 29</sup>

Static Gibbs free energy  $G^*$  may be defined by

$$G^* = F^* - V_0 \bar{\sigma} \cdot \bar{\epsilon} \quad (14)$$

$$= E_L + nE_d - TS^* - V_0 \bar{\sigma} \cdot \bar{\epsilon}, \quad (15)$$

where  $n$  is a constant. Then, it can be shown that

$$dG^* = -V_0 \bar{\epsilon} \cdot d\bar{\sigma} - S^* dT, \quad (16)$$

where we use  $d\tilde{\epsilon} = d\tilde{\epsilon}_e$  for constant  $n$ . However for the definition of the excess Gibbs energy relation that corresponds to Eqs. (3) and (10), one can choose either

$$dG = dG^* + E_d^b dn, \quad (17)$$

or

$$dG = dF - d(V_0 \vec{\sigma} \cdot \tilde{\epsilon}). \quad (18)$$

Equation (17) maintains a symmetry with Eqs. (3) and (10) and yields

$$dG = E_d^b dn - V_0 \tilde{\epsilon} \cdot d\vec{\sigma} - S^* dT. \quad (19)$$

Then, at constant stress and temperature Eq. (19) becomes

$$E_d^b = (\partial G / \partial n)_{\vec{\sigma}, T}.$$

According to Kovács and Zsoldes,<sup>30</sup> a similar expression for the static Gibbs free energy is first realized by Holder and Granato.<sup>31</sup> In contrast, Eq. (18) yields

$$dG = dG^* + E_d^b dn - V_0 \vec{\sigma} \cdot d(\tilde{\epsilon} - \tilde{\epsilon}_e),$$

where because of  $dn$ ,  $d\epsilon$  is not necessarily equal to  $d\tilde{\epsilon}_e$ . In this paper we shall adopt Eq. (17) because of its symmetry with Eqs. (3) and (10).

Now, the entire range of thermodynamic relations may be developed for solids containing dislocation, but we shall limit our applications to those that are useful for shock loadings.

First, from the identity relation,

$$V = (\partial G^* / \partial P)_{T, n} = (\partial G / \partial P)_{T, n},$$

where  $V$  is the thermodynamic specific volume and  $P$  the hydrostatic pressure, one finds that

$$V = V_e + V_d, \quad (20)$$

where the subscripts  $e$  and  $d$  signify lattice and dislocation, respectively.  $V_e$  is the specific volume of the underlying elastic lattice strain.

Second, from the same identity and Eq. (14), one finds

$$\begin{aligned} V &= \partial G^* / \partial P = \partial F^* / \partial P + V, \\ &= (\partial F^* / \partial V)(dV/dP) + V. \end{aligned}$$

But since  $dV/dP$  is not zero in general, the above equation requires that

$$\partial F^* / \partial V = 0. \quad (21)$$

This means that the free energy  $F^*$  is at an extremum with respect to the specific volume given by Eq. (20). In fact, it is not difficult to show that  $F^*$  is at a minimum with respect to  $V$ . The physical meaning of Eq. (21) is that although dislocations are nonequilibrium defects, the crystal as a whole is in a state of minimum free energy. It al-

so implies because of Eq. (20), that when dislocations are present, the crystal dilates to lower the total free energy to a minimum. This then must be the reason why dislocations, though they are nonequilibrium defects, are so stable in crystals. Since crystals dilate trying to accommodate any number of dislocations until they reach saturation, there is no single equilibrium value of dislocation density. As shown in Ref. 22, an assumption of equilibrium dislocation density leads to an irreconcilable result. A similar difficulty will result if we identify  $E_d$  with  $E_d^b$ .

Third, let  $F^*(n=0) = F^{*0}$  and  $G^*(n=0) = G^{*0}$ . Then, it may be found that

$$F^* - F^{*0} = nE_d - T(S^* - S^{*0}),$$

$$G^* - G^{*0} = nE_d - T(S^* - S^{*0}) - V_0(\vec{\sigma} - \vec{\sigma}^0) \cdot \tilde{\epsilon}_e,$$

where the superscript "0" on  $S^*$  denotes the values when  $n=0$ . But for a given state of stress,  $\vec{\sigma}$  is  $\vec{\sigma}^0$  regardless of the dislocation density. Therefore at constant temperature and stress,

$$G^* - G^{*0} = F^* - F^{*0} = nE_d - T(S^* - S^{*0}). \quad (22)$$

If the free-energy difference ( $G^* - G^{*0}$ ) is considered as a barrier to the production of dislocations, homogeneous melting may be defined as the spontaneous saturation of dislocations due to the vanishing free-energy difference at high temperatures and high pressures.<sup>10, 11</sup> That is, melting occurs when

$$G^* - G^{*0} = 0. \quad (23)$$

Then, on combining Eqs. (22) and (23), one finds the entropy of melting,

$$T(S^* - S^{*0}) = nE_d. \quad (24)$$

This result is identical to that used in Ninomiya.<sup>11</sup> We shall come back to this equation in the discussion of instability under shock loadings.

### III. THERMODYNAMICS OF SHOCK COMPRESSION

In order to apply the formalism developed in Sec. II to shock compression of solids, we need to evaluate the plastic work increment  $dW_p$ . We shall assume for simplicity that a plane shock is propagating in an isotropic solid described by a Lagrangian coordinate  $x$ . Then the total work increment  $dW$  is given by

$$dW = -P_x dV = V_0 P_x d\epsilon_x, \quad (25)$$

where  $P_x$  is the compressive stress in the  $x$  direction and  $d\epsilon_x$  the increment of the Lagrangian strain. For plane shock loadings, it is convenient to introduce deviatoric components as follows<sup>22</sup>:

$$\begin{aligned}\Pi_j &= -P_j + P, \\ e_j &= \epsilon_j - \theta/3, \quad j=x, y, z.\end{aligned}\quad (26)$$

Then Eq. (25) becomes

$$dW = -V_0 P d\theta + V_0 \sum_j \Pi_j de_j, \quad (27)$$

where  $d\theta = d\epsilon_x$  for plane compression.

On combining Eqs. (4) and (27), one finds

$$P = (\partial E^*/\partial V_e)_{S^*, e_j^e} = \rho_0 (\partial E^*/\partial \theta_e)_{S^*, e_j^e}, \quad (28)$$

$$\Pi_j = \rho_0 (\partial E^*/\partial e_j^e)_{S^*, v_e} \quad (29)$$

where  $e$  stands for elastic deformation. Now from the assumed isotropy and Eq. (7), one obtains the incremental relations for the stress components  $P$  and  $\Pi_j$ ,

$$dP = -K d\theta_e + (\partial P/\partial S^*) dS^*, \quad (30)$$

$$d\Pi_j = 2\mu de_j^e + (\partial \Pi_j/\partial S^*) dS^*, \quad (31)$$

where  $\mu$  and  $K$  are the isentropic shear and bulk moduli of the material. Since the entropy change under shock loadings is the order of  $(dV)^3$ , the second terms in the above equations are often ignored. However, we note that the moduli are functions of  $\xi_e$ ,  $S^*$ , and  $n$ .

In dealing with plane shock loadings, it is further convenient to introduce the maximum resolved shear stress  $\tau$  and the plastic shear strain  $\gamma_p$  that are defined by

$$\tau = (\Pi_x - \Pi_y)/2 = (\Pi_x - \Pi_z)/2, \quad (32)$$

$$d\gamma_p = d(e_x^p - e_y^p)/2 = d(e_x^p - e_z^p)/2,$$

$$de_j = de_j^e + de_j^p. \quad (33)$$

The last expression, Eq. (33), is really a new, but standard, assumption about the decomposition of the deviatoric strains into a sum of elastic and plastic increments. Then the substitution of Eqs. (32), (33), and (20) into Eq. (27) yields a new expression for the work increment.

$$\begin{aligned}dW &= -P(dV_e + dV_d) \\ &+ V_0 \sum_j \Pi_j de_j^e + V_0(8\tau/3)d\gamma_p,\end{aligned}\quad (34)$$

where  $dW_p$  can be identified by inspection. Now, gathering up Eqs. (2), (4), (5), (30), (31), and (34), one obtains

$$T dS^* = (8\tau V_0/3)d\gamma_p - E_d^p dn - P V_0 d\theta_d + dQ, \quad (35)$$

$$d\tau = \mu(d\epsilon_x - 2d\gamma_p), \quad (36)$$

$$dP = -K(d\epsilon_x - d\theta_d), \quad (37)$$

where the higher-order terms in  $\tau$  and  $P$  are ignored for simplicity.

A comment is in order about the relation between the thermodynamic specific volume  $V$ , and the average strain  $\theta$ . It is customary to introduce plastic incompressibility as we relate  $\theta$  to  $V$ . However, in our formulation the relation is automatically established because of the kinematic constraint for plane compressions [see Eq. (25)]. Then from the thermodynamic identity, Eq. (19), one finds

$$V_0 d\theta = V_0 d\epsilon_x = dV = d(V_e + V_d).$$

In other geometries, we will not be so fortunate, and we must establish a postulate that relates  $\theta$  to  $V$ , including the average plastic strain. Birkhoff once stressed<sup>32</sup> that the difference between the average strain and the thermodynamic specific volume is not a trivial matter. The difference may play an important role in strongly nonequilibrium processes involving volume changes.

To complete the thermodynamic relations, we need the expressions for the increments of dislocation dilatation and the energy  $E_d^p$ . Here, in view of its success in describing melting, we shall use those found in the Ninomiya model.<sup>11</sup> Then, it is found that

$$d\theta = \frac{\alpha}{4\pi} \frac{b_0^3}{v_0} \frac{\mu}{K} (2\Gamma - \frac{2}{3}) dC_d = \beta dC_d, \quad (38)$$

$$E_d^p dn = \left[ \frac{\alpha}{4\pi} \left( \frac{b_0^3}{v_0} \right) \mu N v_0 - \lambda N k T \right] dC_d = \delta dC_d, \quad (39)$$

where  $\alpha$  is a constant related to the crystal structure of the solid,  $b_0$  the length of Burger's vector,  $v_0$  the atomic volume,  $\Gamma$  is the Grüneisen constant,  $C_d$  ( $b_0 N C_d = n$ ) the reduced dislocation density in atomic unit,  $N$  the number of atoms per unit mass,  $k$  is the Boltzmann constant, and  $\lambda$  is a constant related to phonon softening due to dislocations. We note, however, that the above expressions contain only dominant terms in the Ninomiya model.

Although the thermodynamic relations, Eqs. (35)–(39), are our prime concern, they are not sufficient to provide a complete description of dynamic problems. We must include the equations for the conservation of mass and linear momentum and other mechanical constitutive relations for  $\tau$ ,  $\gamma_p$ , and  $n$ . The equation for the conservation of mass is

$$\partial \epsilon_x / \partial t = \rho_0 \partial V / \partial t = \partial u / \partial x,$$

where  $u$  is the material particle velocity. The equation for the conservation of linear momentum is

$$\partial(\rho_0 u) / \partial t = \partial P_x / \partial t = -\partial(P - 4\tau/3) / \partial t.$$

The equation for heat conduction is

$$\partial Q/\partial t = H(\partial T/\partial x, \dots),$$

and for dislocation mechanics and plastic flow,

$$\partial n/\partial t = g(\partial \gamma_p/\partial t, \dots),$$

$$\partial \gamma_p/\partial t = f(\tau, \gamma_p, P, \dots).$$

We see in the above equations an interesting interaction between shear and hydrostatic pressure through dislocation dynamics whose features are similar to pressure-sensitive dilatancy in rocks.<sup>33, 34</sup> But in this paper we shall restrict our attention to the thermodynamic relations, in particular, the entropy relation that is usually ignored in shock-wave mechanics.<sup>14</sup> It contains a stability condition for dissipative plastic flow similar to those discussed by Glansdorff and Prigogine.<sup>26</sup>

Following usual conventions we shall ignore thermal conduction. Then, Eq. (35) yields the irreversible internal entropy production,

$$T dS^* = (8\tau V_0/3) d\gamma_p - (PV_0\beta + \delta) dC_d, \quad (40)$$

where  $\beta$  and  $\delta$  are given by Eqs. (38) and (39), respectively. Since the irreversible entropy production cannot be negative, there exists a critical condition given by

$$(8\tau V_0/3) d\gamma_p = (PV_0\beta + \delta) dC_d. \quad (41)$$

This condition seems to have escaped our attention so far because of the usual approximation that the dislocation dilatation is small for normal dislocation density in mechanical flow. But the product  $PV_0\beta$  is not necessarily negligible for strong shocks.

Explicit evaluation of the critical condition requires knowledge about the relation between  $\gamma_p$  and  $C_d$  which is, according to Gilman,<sup>15</sup> not available for the entire range of our interest. But useful information may be obtained by a polynomial relation,<sup>15</sup>

$$n = b_0 NC_d = M\gamma_p + \text{constant}, \quad (42)$$

where  $l$  and  $M$  are constant. Then, Eq. (40) becomes

$$T dS^* = [8\tau V_0/3 - (PV_0\beta + \delta) LM\gamma_p^{l-1}/b_0 N] d\gamma_p. \quad (43)$$

Now, the critical condition becomes

$$8\tau V_0/3 = (PV_0\beta + \delta) LM\gamma_p^{l-1}/b_0 N. \quad (44)$$

Equation (43) shows that if  $dS^*$  remains positive finite for nonvanishing plastic flow  $d\gamma_p$ , then the condition (44) can be interpreted as that for the onset of unconfined flow (adiabatic shearing) in which  $d\gamma_p$  increases to infinity. Finally, it is reminded that  $\gamma_p$  is the plastic strain in the plane of

maximum shear.

As noted above, not all the data are available for evaluation of Eqs. (41) or (44). Hence we shall look at the features of Eqs. (41) and (44) using the smallest number of assumptions. One way of doing this is to introduce a parameter  $a$  which expresses the fraction of plastic work that transforms into the creation of dislocations. In normal plastic flow this fraction is known to vary from 5 to 15%.<sup>35</sup> But locally this fraction could be greater than that observed in normal plastic flow.

In terms of the above fraction, Eq. (44) becomes

$$a(8\tau V_0/3) = \delta LM\gamma_p^{l-1}/b_0 N, \quad (45)$$

$$PV_0\beta = (1-a)\delta/a, \quad (46)$$

where  $a$  is the fraction of plastic work that transforms into the dislocation energy. Equation (45) is really the definition of  $a$  and Eq. (46) expresses the reduced critical condition in terms of  $a$ . Then substituting Eqs. (38) and (39) into Eq. (46), one finds the critical pressure  $P_c$  in terms of temperature  $T$ .

$$P_c = [(1-a)/a] \left\{ K/(2\Gamma - \frac{2}{3}) - (4\pi/\alpha) \right. \\ \left. \times [\rho_0 N k \lambda / (2\Gamma - \frac{2}{3})] (v_0/b_0^3) (K/\mu) T \right\}. \quad (47)$$

We note that this equation can be derived without the polynomial relation, Eq. (42).

An important feature of Eq. (47) is that the critical pressure decreases from its value at the absolute zero temperature to the value at some melting temperature. If, however, the shear modulus  $\mu$  vanishes at the melting temperature as mechanical theories of melting suggest,<sup>25</sup> the critical pressure reaches zero before the melting temperature. Then, the adiabatic shear instability always precedes the thermodynamic melting prescribed by Eq. (23). Hence, as some mechanical theories hypothesize that melting would occur in the form of a large shearing displacement,<sup>36, 37</sup> it is possible that the above instability serves as a dynamic intermediary between temperature-dependent shear moduli and the thermodynamic melting defined by the equality  $G^* = G^{*0}$ . Furthermore, in terms of the entropy difference ( $S^* - S^{*0}$ ), there appear to be three paths for reaching a saturation dislocation density as shown in Fig. 1. The figure shows that although the final state may be the same disordered state, the thermodynamic melting ( $G^* = G^{*0}$ ) and the mechanical instability are not necessarily the same phenomenon.

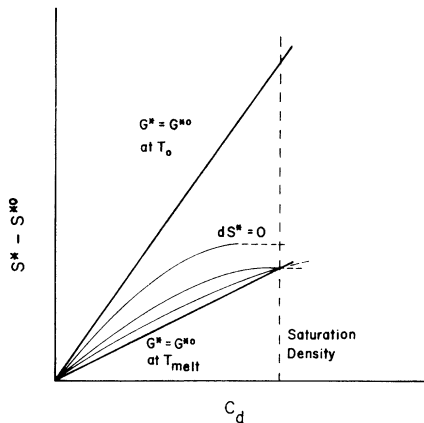


FIG. 1. According to Eq. (24), a spontaneous saturation of dislocations occurs when the static entropy difference ( $S^* - S^0$ ) intersects the line defined by the equality relation  $G^* = G^0$  at the melting temperature  $T_{\text{melt}}$ . However, under dynamic conditions the saturation can occur as a result of violation of the condition that  $dS^* > 0$  for irreversible processes. The critical state is given by the relation  $dS^* = 0$ .

#### IV. EXAMPLES

We shall now examine the critical conditions for adiabatic shearing for selected materials from oxides and metals. The former are well suited for assuming the adiabatic condition ( $dQ = 0$ ) and are known to melt under shock loadings.<sup>6,3</sup> Although metals are good thermal conductors, they are included because of their observed adiabatic shearing<sup>8</sup> and extensive information on dislocation dynamics.<sup>14,15</sup>

A simple, but informative representation of the critical conditions, Eq. (47), is the drawing of the critical curves in the pressure-temperature space in terms of the important parameters associated with dislocations;  $a$  and  $\lambda$ . The former is the fraction of plastic work that is converted into dislocation energy and the latter is the phonon mode softening due to dislocations. In our examples we shall assume for simplicity (1) that shear moduli vanish at the melting temperature following a parabolic function,<sup>25,38</sup>

$$\mu = \mu_0(1 - T/T_m)^2,$$

where  $\mu_0$  is the shear modulus at  $T = 0$  and  $T_m$  is the melting temperature, and (2) that other variables are constants. This assumption should not alter the qualitative features of the critical curves defined by Eq. (47). As is discussed in Ref. 22, accurate determination of elastic moduli is a task by itself and should be done in conjunction with the reevaluation of Eqs. (38) and (39). It is hoped that such an analysis will also remove the singularity

TABLE I. Material constants.<sup>a</sup>

	SiO <sub>2</sub>	MgO	Fe( $\alpha$ )
$\rho_0$ (10 <sup>3</sup> kg/m <sup>3</sup> )	2.65	3.57	7.87
$K_0$ (GPa)	37.6	165	168.3
$\mu_0$ (GPa)	44.7	117.2	81.5
$Nk$ (J/K)	0.138	0.207	0.149
$\Gamma$	1	1.4	1.7
$b_0^3/v_0$	$\sqrt{2}$	$\sqrt{2}$	$3\sqrt{3}/4$
$T_m$ (K)	1986	3223	1808
$\alpha$	0.9	0.9	0.9

<sup>a</sup>The data are assembled from (1) R. G. McQueen, J. N. Fritz, and S. P. Marsh, *J. Geophys. Res.* **69**, 2947 (1964); (2) S. P. Clark, Jr., *Handbook of Physical Constants*, edited by S. P. Clark, Jr. (Yale University Press, New Haven, 1966); (3) E. Domany *et al.*, *J. Geophys. Res.* **80**, 4851 (1975); (4) K. A. Gschneider, Jr., *Solid State Phys.* **16** (Academic, New York, 1964), p. 276; (5) T. Ninomiya, *J. Phys. Soc. Jpn.* **44**, 263 (1978).

in Eq. (47) that occurs when the Grüneisen constant is  $\frac{1}{3}$ . The material constants used are summarized in Table I.

Figures 2–4 show representative examples of the critical curves for SiO<sub>2</sub>, MgO, and Fe( $\alpha$ ). The fraction  $a$  is set arbitrarily at 10%, 30%, and 50%. The values of  $\lambda$  are taken from Ninomiya

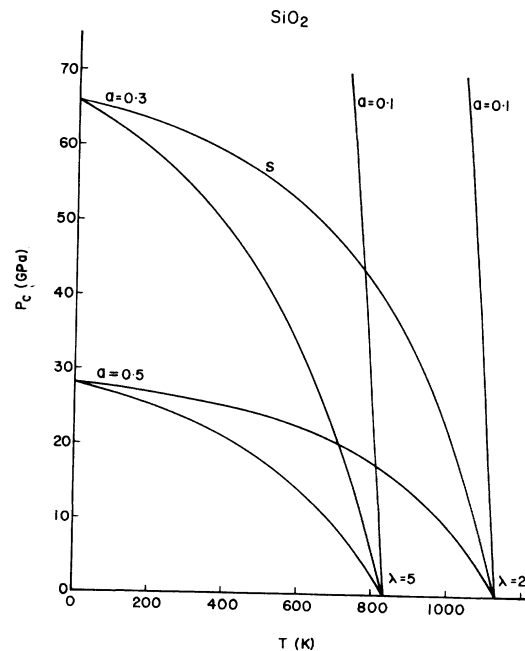


FIG. 2. Calculated critical lines for SiO<sub>2</sub> in terms of the two important dislocation parameters:  $a$  and  $\lambda$ . The curves indicate the state of critical pressure  $P_c$  and temperature at which the principle of positive-entropy production for plastic flow is violated. For instance, if  $a = 0.3$  and  $\lambda = 2$ , then the critical state is given by curve S.

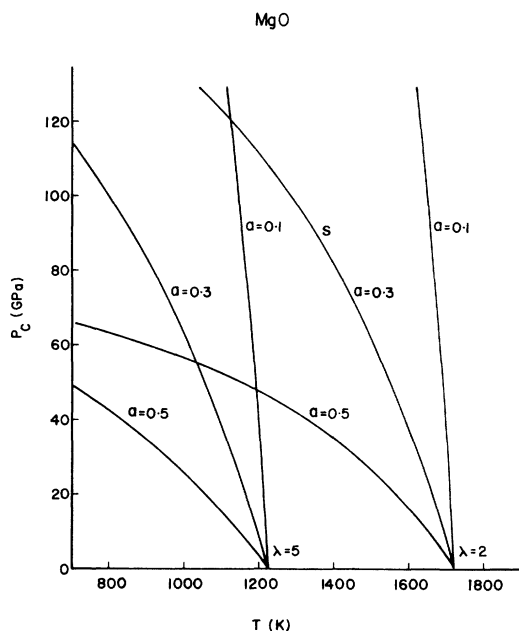


FIG. 3. Calculated critical lines for MgO in terms of the two important dislocation parameters:  $a$  and  $\lambda$ . The curves indicate the state of critical pressure  $P_c$  and temperature at which the principle of positive-entropy production for plastic flow is violated. For instance, if  $a = 0.3$  and  $\lambda = 2$ , then the critical state is given by curve S.

ya<sup>11</sup> and Nabarro<sup>39</sup> and seem to vary from 2 to 5 depending upon the model used. In these figures the intersections with the abscissa are controlled by  $a$ , the fraction of plastic work that is transformed into dislocation energy, and the ones with the ordinate by  $\lambda$ , the phonon mode softening. One can easily discern general features of the critical curves: (1) If the pressures are high enough, adiabatic shearing can occur at very low temperatures. Such examples are speculated in a tungsten alloy, aluminum alloys, and pure titanium.<sup>8</sup> (2) If the parameter  $a$  remains about 10%, the instability is practically temperature controlled regardless of material and occurs at about half the melting temperature. (3) As is expected from Eq. (47), the critical pressure decreases as the temperature increases. This feature is particularly strong in iron.

For iron we find that the theoretical results are not inconsistent with experimental observation<sup>8</sup>: "Shear bands are generally considered to result from the local temperature exceeding the normal  $\alpha$  to  $\gamma$  transformation temperature although the effect of pressure is thought by many to lower the transformation temperature." But there is not yet an accurate measurement of temperature in such bands.

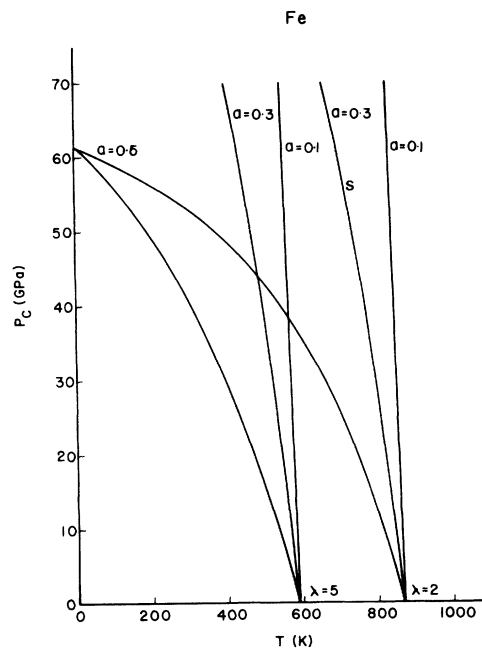


FIG. 4. Calculated critical lines for Fe( $\alpha$ ) in terms of the two important dislocation parameters:  $a$  and  $\lambda$ . The curves indicate the state of critical pressure  $P_c$  and temperature at which the principle of entropy production for plastic flow is violated. For instance, if  $a = 0.3$  and  $\lambda = 2$ , then the critical state is given by curve S.

In the case of quartz, the theoretical curves are again consistent with both experimental observations<sup>3,5,6</sup> and an alternative theoretical model of instability.<sup>6</sup> In view of Fig. 1, we may suggest that the dynamic melting can proceed within a submicrosecond because of shear yielding under dynamic loadings, and that as Teller suggested,<sup>6,40</sup> rather than direct shear activation, dissipative energy accumulation aids the transition.

Klein<sup>4</sup> observed shock lamellae in single-crystal MgO at shock stresses near 8 GPa, and the lamellae are usually attributed to unstable shear yielding. But at the moment it is not certain whether they reached the state described by Eq. (47). Furthermore, we need the critical conditions similar to Eq. (47) that are applicable for single crystals under shock loadings. Nevertheless, the conditions shown in Fig. 3 are not inconsistent with those speculated for minerals.<sup>6,2</sup>

As mentioned earlier, Eq. (46) is necessary for the instability resulting from the violation of positive-entropy production but in our approximation not sufficient. An additional condition given by Eq. (45) must be satisfied for the onset of the instability. When  $l = 1$ , the latter equation becomes independent of the plastic strain and yields

$$a(8\tau V_0/3) = \delta M / b_0 N, \quad (48)$$

TABLE II. Dislocation multiplication coefficients.<sup>a</sup>

	Al (fcc)	Cu (fcc)	Fe (bcc)	W (bcc)
M (dynamic) ( $10^{13}/\text{m}^2$ )	2,060	3,200	3,270 (5,450) <sup>+</sup>	1,700
M (after Gilman) ( $10^{13}/\text{m}^2$ )	80	2~100	33~250	
$\rho_0$ ( $10^3 \text{ kg}/\text{m}^3$ )	2.7	8.96	7.87	31.4
$\mu_0$ (GPa)	26.6	45.1	81.5	153
$b_0^3/\nu_0$	$\sqrt{2}$	$\sqrt{2}$	$3\sqrt{3}/4$	$3\sqrt{3}/4$
$\tau$ (GPa) (from HEL)	0.045	0.298	0.552 (0.92) <sup>+</sup>	3.14
$b_0$ (Å)	2.93	2.55	2.53	1.38
$10^{22}$ (N)	2.232	0.948	1.078	0.3277

<sup>a</sup>The data are assembled from the sources listed in Table I and Ref. 14.

where  $n = M\gamma_p + \text{constant}$ . Hence, if the shear stress  $\tau$  (which is really the shear strength) is known, Eq. (48) provides the dislocation multiplication coefficient  $M$  discussed in Gilman.<sup>15</sup> However, the evaluation of  $\tau$  over a wide range of temperature, pressure, and dislocation density is not a simple matter and not available at the moment. But in shock compression  $M$  may be estimated on the basis of  $\tau$  calculated from the Hugoniot elastic limit.

Table II lists the results with the material coefficients used in the calculation of the critical curves in Figs. 2–4. However, we did not determine  $M$  for the oxides because of the lack of comparable experimental values. Nevertheless, we expect them to be comparable with those for the

metals in Table II. As anticipated, the dynamic  $M$  are much greater than the quasistatic values quoted in Gilman,<sup>15</sup> and are of the order of  $10^{15}$  per square meter. According to Eq. (42), they yield the dislocation density of the same order (if not slightly higher) for the plastic strain of, say, 10–20%. But these magnitudes are precisely what were observed in the slipped regions of shock-loaded crystals<sup>41,42</sup> or in the region of tangled dislocation dipoles at large plastic strains.<sup>43</sup> Furthermore, the same order of density is found for the shock-loaded aluminum to 10 GPa from an alternative thermodynamic calculation.<sup>22</sup> Hence we may imply from the above numerical results that the condition imposed on the dislocation density at the onset of adiabatic shearing (or heterogeneous melting) are again not inconsistent with those observed or speculated from other analyses. We may then suggest that the instability resulting from a violation of positive-entropy production can occur under shock compression and that depending upon available times under the loading, it can lead to saturation of dislocations. In the case of isotropic solids the instability occurs in the plane of maximum shear. Hence, we speculate that shear bands such as those seen in a microphotograph of the anorthite<sup>2</sup> shocked to 30 GPa are caused by this instability.

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