

Capillary Equilibria of Dislocated Crystals

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It is shown that a dislocation whose Burgers vector exceeds a critical value, of the order of magnitude 10 Å., is only in equilibrium with an empty tube at its core. This is not the case in metals or other simple crystalline solids, but is likely to be the case in protein crystals, which therefore, unfortunately, do not provide good models of simple crystalline substances in respect of dislocations. The same causes generally give rise to a dimple or crater where a dislocation meets a free surface, and the shape of this crater is calculated. Though shallow in form, it is infinitely deep except at a habit face of a crystal, where it is of finite depth and may be totally absent.

1. The equilibrium of open-cored dislocations

It will be shown that for a dislocation of large Burgers vector* there exists a state of equilibrium in which the core of the dislocation is an empty tube. We shall find, however, that this is not the case for the elementary dislocations of a typical metal or simple ionic crystal; but it may be so for substances with large unit cells, of the order of 10 Å. or more, e.g. some silicates. It will assuredly be the case in protein crystals.

For simplicity we consider the case of a screw dislocation in a material with isotropic elastic constants. Strain-energy densities are of similar magnitude at similar distances from dislocations of other orientation and in materials of naturally occurring degrees of anisotropy in their elastic behaviour. Let there be an empty cylinder of radius r , the dislocation line lying in the cylinder. Then the shear strain at the surface of the cylinder is $b/2\pi r$, where b is the modulus of the Burgers vector. There is consequently a strain-energy density here of $\mu b^2/8\pi^2 r^2$, where μ is the rigidity modulus.

Suppose that a shell of material of thickness dr evaporates from this cylinder and deposits elsewhere, on a surface of the material whose radius of curvature is negligibly large. The interior cylindrical surface is thus enlarged. If γ is the specific surface free energy of the

* The Burgers vector is the name we give to what Burgers (1939) called the 'strength' of a dislocation. This vector is parallel to the dislocation line in a 'screw' and normal to it in an 'edge' dislocation, these being only particular cases of the general situation. A simple account of the geometry and elastic fields of dislocations is given by Cottrell (1949).

substance, the total increase in free energy per unit length of cylinder is

$$dF = 2\pi\gamma dr - (\mu b^2/8\pi^2 r^2) 2\pi r dr. \quad (1)$$

There is an equilibrium when dF/dr is zero, i.e. when

$$r = \mu b^2/8\pi^2 \gamma. \quad (2)$$

Now, empirically the rigidities and surface energies of substances tend to vary in a parallel manner so that γ/μ is very roughly a constant length (cf. Table 1), a typical value being say $\frac{1}{4}$ Å. In consequence r is less than 1 Å. unless b exceeds 4–5 Å. The implied assumption of linear elasticity is then invalid. If b were as large as 100 Å., as would be appropriate in protein crystals, this objection would disappear, and we may conclude that the typical dislocation in such a crystal would, in equilibrium, have a hollow core of the order of 1000 Å. in diameter. This brings the unfortunate conclusion that these crystals, the ones in which we can most easily see the constituent parts, do not furnish satisfactory analogues of simpler crystals with regard to dislocations.

Let us now make an approximate allowance for the non-linear elastic behaviour. We shall assume that stress is related to strain by Hooke's law up to a strain of 0.1 and thereafter is constant (as in Figs. 1 (ii) and 2 (ii)). The strain-energy density is

$$\left. \begin{aligned} \mu b^2/8\pi^2 r^2 & \quad (r \geq 5b/\pi); \\ \mu b/20\pi r - \mu/200 & \quad (r \leq 5b/\pi). \end{aligned} \right\} \quad (3)$$

Table 1. *Approximate rigidities and surface energies of solids*

Substance	Rigidity modulus μ (10^{11} erg cm. ⁻²)	Surface energy γ (erg cm. ⁻²)	γ/μ (10^{-8} cm.)	Reference
Copper	4.4	1400	0.32	Udin <i>et al.</i> (1949)
Sodium chloride	1.5	155	0.10	Rose (1936), Shuttleworth (1949)
Argon	0.106	42	0.40	Mackenzie & Mott (1950), Shuttleworth (1949)
Mica	8.0	4500 (<i>in vacuo</i>) 400 (<i>in air</i>)	0.56 0.05	Obreimoff (1930) Orowan (1933)

Then for $r < 5b/\pi$, (1) is replaced by

$$dF = 2\pi\gamma dr - (\mu b/20\pi r - \mu/200) 2\pi r dr, \quad (4)$$

i.e. $dF/dr = 2\pi\gamma - \mu b/10 + \pi r\mu/100,$ (5)

giving an equilibrium at

$$r = 10b/\pi - 200\gamma/\mu. \quad (6)$$

There can be no equilibrium with finite r unless

$$b > 20\pi\gamma/\mu. \quad (7)$$

This condition is perhaps not strict enough. If we assume a more extreme non-linearity of the elastic behaviour (as in Figs. 1 (iii) and 2 (iii)), such that for strains greater than 0.1 the strain-energy density remains constant (at $\mu/200$), then we have for $r \leq 5b/\pi$:

$$dF/dr = 2\pi\gamma - 2\pi r\mu/200. \quad (8)$$

The smallest value of dF/dr occurs at $r = 5b/\pi$ and is positive unless

$$b > 40\pi\gamma/\mu. \quad (9)$$

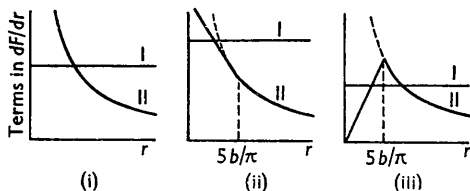


Fig. 1. Forces tending to contract and enlarge a hole round a dislocation: (I) arising from surface energy, $2\pi\gamma$; (II) arising from strain energy, $\mu b^2/4\pi r$ in (i) and modified for non-linear elastic behaviour on two extreme approximations in (ii) and (iii).

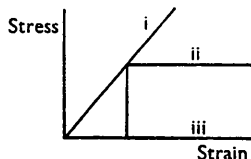


Fig. 2. Approximations to the stress-strain law assumed in the three cases of Fig. 1.

If this condition is satisfied, there are two positions of equilibrium with finite r , a stable one (given by (2)) for $r > 5b/\pi$ and an unstable one for $r < 5b/\pi$. The stable equilibrium is less stable than the condition $r = 0$ unless (as one finds by integrating dF/dr)

$$b > 40e^{1/2}\pi\gamma/\mu = 66\pi\gamma/\mu. \quad (10)$$

Thus if $\gamma/\mu = 0.1$ Å. the assumptions leading to (7) and (10) respectively indicate critical values of 7 or 20 Å. above which a dislocation in equilibrium will be open-cored.

We may treat our problem more generally as follows: If the free-energy density due to strain is a function $E(\epsilon)$ of the strain ϵ , and the specific surface free energy is likewise a function $\gamma(\epsilon)$, the increase of free energy per unit length of dislocation, from the fully closed condition to that with an empty core of radius r_1 , is

$$F(r_1) = \int_0^{r_1} [2\pi\gamma(\epsilon) - 2\pi r E(\epsilon)] dr \\ = \int_0^{\epsilon(r_1)} [2\pi\gamma(\epsilon) dr/d\epsilon - 2\pi r E(\epsilon) dr/d\epsilon] d\epsilon. \quad (11)$$

Introducing $\epsilon = b/2\pi r$, this becomes

$$F(r_1) = \int_{b/2\pi r_1}^{\infty} [b\gamma(\epsilon)/\epsilon^2 - b^2 E(\epsilon)/2\pi\epsilon^3] d\epsilon. \quad (12)$$

An equilibrium exists at a value of r_1 where the integrand becomes zero; this represents a more stable state than the fully closed condition if the integral is then negative. The generalization is a somewhat empty one, while we can make only rough guesses at the functions involved. The assumption, implied earlier, that $\gamma(\epsilon)$ is constant is not an unreasonable approximation in view of the fact that solids and their melts have much the same surface energy.

In spite of uncertainties of approximate theory and of essential data it is fair to conclude that dislocations in thermodynamic equilibrium will have open cores in protein crystals, but never in metal crystals, while some silicate crystals with lattice spacings of the order of 10 Å. form borderline cases. Beryl, for example, has lattice spacings of approximately 9 Å. This is the minimum possible Burgers vector in the basal plane (though a Burgers vector of half the lattice spacing parallel to the hexad axis might well be possible). It is at least an acceptable possibility that dislocations in this crystal may be hollow. It is to be borne in mind that when a crystal grows in a solvent medium, γ is to be decreased by the 'heat of wetting' of the crystal; this enhances the stability, likelihood of occurrence, and diameter of hollow dislocations.

2. End craters and end dimples of dislocations

A related problem is that of determining the form of the dimple or crater which should occur where a dislocation meets the free surface of a crystal. To simplify the problem we shall assume a strain-energy density around the dislocation, at the surface, which has circular symmetry and is the same as that around the dislocation in the interior. This is never actually true, the first assumption being violated for an edge and the second for both, most seriously for a screw dislocation. The violation of the second assumption is less serious than immediately appears, since for any displacement of the surface wherein it remains parallel to itself, the special stress distribution near to the surface shifts with the surface, and it is the volume which has the asymptotic stress distribution at depth which alters.

The simplest way to interpret the equilibrium form of the crystal surface which should result is to regard the strain-energy density as a pressure, directed inwards towards the material, which balances a pressure directed outwards arising from the surface energy, interpreted as a surface tension in the manner customary with fluids. The validity of either substitution of concepts is readily established by expressing the consequences of either in differential form. The surface must therefore be everywhere concave, the concavity diminishing as $1/r^2$

at a distance from the dislocation. When $E(r)$ is the strain-energy density, there is equilibrium when

$$\gamma(1/R_2 - 1/R_1) = E(r) \quad (13)$$

$$= r_0\gamma/r^2, \quad (14)^*$$

R_1 and R_2 being the two principal radii of curvature shown in Fig. 3 and

$$r_0 = b^2\mu/8\pi^2\gamma \quad (15)$$

being the equilibrium radius of equation (2), corresponding to $E(r) = \mu b^2/8\pi^2 r^2$. Here, and below, we write equations with two right-hand sides, for brevity, the first being the more general form and the second valid at large r . Now

$$R_2 = r[1 + (dz/dr)^2]^{1/2} / (dz/dr) \quad (16)$$

$$= r[1 + (dr/dz)^2]^{1/2}, \quad (17)$$

while $R_1 = -[1 + (dz/dr)^2]^{3/2} / (d^2z/dr^2) \quad (18)$

$$= [1 + (dr/dz)^2]^{3/2} / (d^2r/dz^2). \quad (19)$$

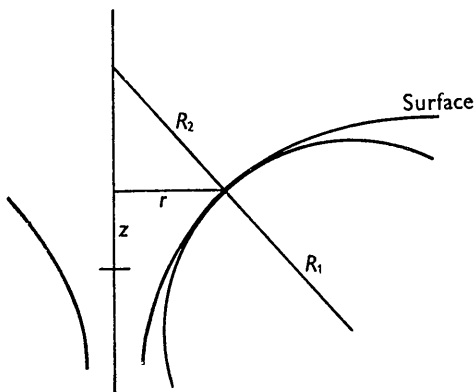


Fig. 3. Co-ordinates and principal curvature radii for a surface crater.

Substituting in (13), (14) we obtain either

$$\frac{dz/dr}{r[1 + (dz/dr)^2]^{1/2}} + \frac{d^2z/dr^2}{[1 + (dz/dr)^2]^{3/2}} = \frac{E(r)}{\gamma} = \frac{r_0}{r^2} \quad (20, 21)$$

or $\frac{1}{r[1 + (dr/dz)^2]^{1/2}} - \frac{d^2r/dz^2}{[1 + (dr/dz)^2]^{3/2}} = \frac{E(r)}{\gamma} = \frac{r_0}{r^2}. \quad (22, 23)$

When dz/dr is small, we may reduce (20) and (21) to

$$r^2 d^2z/dr^2 + rdz/dr = r^2 E(r)/\gamma = r_0, \quad (24, 25)$$

and when dr/dz is small, we may reduce (22) and (23) to

$$r^2 d^2r/dz^2 - r = -r^2 E(r)/\gamma = -r_0. \quad (25, 26)$$

The substitution $r = r_1 e^\theta$, where r_1 is any arbitrary constant length, brings equation (25) into the form $d^2z/d\theta^2 = r_0$, whence

$$dz/dr = (r_0/r) \ln(r/r_1) + A/r, \quad (27)$$

$$z = \frac{1}{2} r_0 [\ln(r/r_1)]^2 + A \ln(r/r_1) + B. \quad (28)$$

It is apparent that we cannot determine either integration constant A or B from a boundary condition at infinity.

* A referee found it illuminating to note here that the surface thus defined is also the equilibrium surface of a liquid containing a vortex, when the equilibrium is determined by surface tension rather than by gravity.

In the ordinary case of a closed-core dislocation, if we assume that within the radius $5b/\pi$ the strain-energy density is constant and equal to $\mu/200$, then the surface in capillary equilibrium in this region is a sphere of radius

$$\rho = 400\gamma/\mu, \quad (29)$$

or, for small r , $z = z_0 + \mu r^2/800\gamma. \quad (30)$

The surfaces within and without $r = 5b/\pi$ must join smoothly there. Equating values of dz/dr

$$\frac{\pi r_0}{5b} \ln\left(\frac{5b}{\pi r_1}\right) + \frac{\pi A}{5b} = \frac{b\mu}{80\pi\gamma} = \frac{\pi r_0}{10b}. \quad (31)$$

A is thus made to vanish by choosing for the arbitrary length r_1

$$r_1 = 5b/\pi e^{1/2} = 0.966b. \quad (32)$$

Then, choosing B so that $z = 0$ when $r = 5b/\pi$, we have in place of (28) $Z = \frac{1}{2} r_0 [\ln(\pi e^{1/2} r/5b)]^2 - \frac{1}{8} r_0. \quad (33)$

This expression (together with the central spherical cup defined by (30)) can be considered to give a tolerable approximation for $b < 20\pi\gamma/\mu$ (which ensures that dz/dr never exceeds $\frac{1}{2}$). This requirement is well satisfied in the metals and other simple crystals.

The behaviour of (33) at infinity is a striking example of the fact that only an infinite perfect crystal can be in equilibrium with an infinite perfect crystal; a single dislocation in one of them causes evaporation to make a crater which, though shallow in form, is of infinite volume and depth.

Equation (27) may be obtained by direct physical argument, by equating the vertical resultant force arising from 'surface tension' around a circle of radius r to the 'line tension' of the dislocation, taking into account for the latter only the elastic energy contained in a cylinder of the same radius r . Derived in this way, it is not immediately obvious that the equation is an approximation, but the case of the open-cored dislocation suffices to show that it is.

For the open-cored dislocation we may use (26) to discuss the manner in which the tube begins to widen as the surface is approached. The equation is reduced by substituting p for dr/dz , and we then obtain

$$dr/dz = (2 \ln r + 2r_0/r + 2A)^{1/2}.$$

A is determined from the boundary condition deep down the tube, namely, $dz/dr = 0$, $r = r_0$. Hence

$$dr/dz = [2 \ln(r/r_0) - 2(1 - r_0/r)]^{1/2} \quad (34)$$

$$= \frac{r - r_0}{r_0} \left[1 - \frac{4}{3} \left(\frac{r - r_0}{r_0} \right) + \frac{3}{2} \left(\frac{r - r_0}{r_0} \right)^2 - \dots \right]. \quad (35)$$

When $(r - r_0) \ll r_0$, we may take the square-bracket series to be 1 and obtain

$$(r - r_0) = e^{2z/r_0}, \quad (36)$$

so that the tube widens exponentially to begin with.

There follows a large gap in which we cannot use the approximations leading either to (36) or to (28), while equations (21) and (23) are intolerable. We may, however, go back to equation (14),

$$1/R_1 = 1/R_2 - r_0/r^2, \quad (37)$$

and construct the solution in small successive arcs with ruler and compasses. All calculations involved may be performed geometrically (see Fig. 4).

The profile shown in Fig. 5 was constructed in this way, aiming only at moderate accuracy. It was drawn with nine successive centres to cover the range $dr/dz = 0.1$ to 0.25 , starting with $z=0$, $r=1.1r_0$, $dr/dz=0.1$, $R_1=10r_0$. For larger r it may be continued with

$$z/r_0 = \frac{1}{2}[\ln(4r/3r_0)]^2 + 4.3, \quad (38)$$

which is of the form (28) and fits the constructed curve admirably from $r/r_0=8$ onwards. The slope $\frac{1}{2}$ occurs at $r/r_0=10.5$, $z/r_0=7.8$. The slope 1 occurs at $r/r_0=3.0$, $z/r_0=4.3$. The latter could be usefully chosen as a new zero of z , eliminating the constant term from (38).

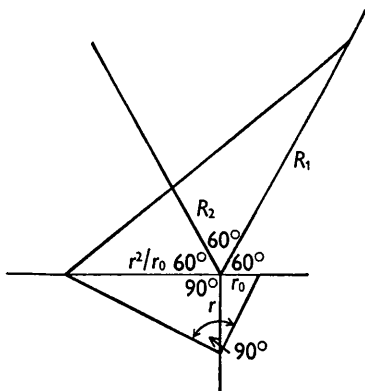


Fig. 4. Nomographic construction for $1/R_1 = 1/R_2 - r_0/r^2$.

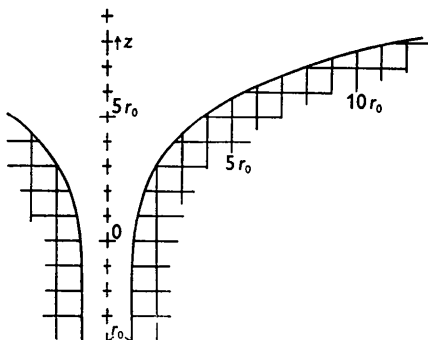


Fig. 5. The surface crater at the end of a hollow dislocation, if surface energy is independent of orientation.

3. Close-packed surfaces

In our treatment above we assume that the surface of the material is infinitesimally displaceable and that its surface energy is independent of orientation. These assumptions gravely fail in the case of close-packed or 'saturated' crystal faces, at the orientation of which there is a sharply cusped minimum of surface energy, and whose properties do not recur in displacement until an entire molecular layer has been added or removed. Wherever the crater surface becomes tangential to such a surface as this, it will be flattened. This is not im-

portant except in the particular and interesting case in which the flat face itself which the dislocation meets is such a surface (generally speaking, a habit face of the crystal). Now, supposing the Burgers vector of the dislocation is parallel to the free surface (i.e. it is an edge dislocation), the crater, if any is formed, must be in fact an amphitheatre of monomolecular steps, and instead of discussing the equilibrium of a displaceable surface we should discuss the equilibrium of closed loops of step line around the end of the dislocation. On the assumptions which we have made this becomes virtually the same problem as the first one we considered, the equilibrium of a cylindrical surface. If we go on to assume that the line energy of a monomolecular step is equal to surface energy times step height, the problems become identical. Then if the dislocation core is filled in equilibrium, there is likewise no surface crater, and if there is a hollow core it is a well of uniform diameter, right up to the surface. In fact (except at the absolute zero of temperature) entropy terms will lower the edge-free energy of a step, as a result of which surface craters may appear with closed-core dislocations, and when the dislocation has an open core the entrance to the tube will be a rounded one. But the divergent behaviour at infinity is now eliminated; the crater on a close-packed surface will be of finite (if not zero) depth and volume for an edge dislocation.

The case of a screw dislocation ending at a close-packed surface is different. There is now an inevitable step line running outwards from the end of the dislocation (cf. Frank, 1949). In this case the rotationally averaged surface is virtually capable of infinitesimal displacements by displacements of the spiral step line on the helicoidal surface of the crystal. It is best to discuss the equilibrium in terms of the equilibrium form of this spiral. We shall assume the temperature to be sufficiently high for the specific free energy per unit length of a step, γ' , to be regarded as a constant independent of orientation. The main conclusion we reach will be still stronger at temperatures at which the step-line adheres to particular crystallographic directions. If a is the step height, the equilibrium curvature, $1/\rho$, will be given by

$$\gamma'/\rho = aE(r) = ab^2\mu/8\pi^2r^2, \quad (39)$$

i.e. $\rho = r^2/k,$ (40)

where $k = ab^2\mu/8\pi^2\gamma'$ (41)

is a length essentially similar to r_0 , above. Since $\rho \gg r$ pretty well as soon as $r > b$, the curvature considered here is always negligible compared with the curvatures of step lines, due to supersaturation, which are considered in the theory of crystal growth.

At large r , $\rho \gg r$, and the line therefore becomes approximately radial. Let ψ be the angle which the line makes with the radius vector, and p be the distance between the origin and the tangent to the line. Let α and s be intrinsic co-ordinates of the line, while r and θ

are polar co-ordinates. Then, subject to the approximations which become valid when the line is nearly radial,

$$\frac{dp}{dr} = \frac{dp}{ds} = r \frac{d\alpha}{ds} = \frac{r}{\rho} = \frac{k}{r}.$$

Hence
$$p = k \ln(r/l). \quad (42)$$

Further,
$$\frac{d\theta}{dr} = \frac{d\theta}{ds} = \frac{\psi}{r} = \frac{p}{r^2} = \frac{k}{r^2} \ln\left(\frac{r}{l}\right).$$

Hence
$$\theta = \theta_\infty - (k/r) \ln(er/l). \quad (43)$$

Now $z = b\theta/2\pi$, so that (43) may be compared with (28). The divergence at infinity has been eliminated. $\theta(r)$, the unknown exact solution of the differential equation (40), of which (43) is the asymptotic form at large r , involves two integration constants, θ_∞ and l . According to the choice of these, $\theta(r)$ describes a great variety of forms of the step line, including those (with large l) which are nearly straight and pass nowhere near the

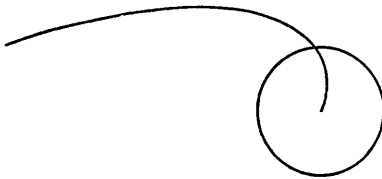


Fig. 6. An equilibrium step line ending on a dislocation with no crater.



Fig. 7. An equilibrium step line ending at a crater.

dislocation. We require l to be chosen in such a way that the step line ends on the dislocation. If the dislocation has a hollow core, the step line should joint the mouth of the well tangentially. In the more normal case of a closed core, (40) ceases to hold where Hooke's law fails, which we shall take as before to be at the radius $5b/\pi$. It has little meaning to represent the step-line as a smooth curve within this region, but in so far as it has any it should be a circular arc leading to the centre, whose radius of curvature is $25b^2/\pi^2k = 200\gamma'/a\mu$. The requirement that the spiral $\theta(r)$ should join smoothly on to this arc as in Fig. 6 will fix the integration constants.

There is another region in which we may obtain approximate analytical solutions to (40), namely, where $dr/d\theta$ is negligible compared with r , when the equation reduces to

$$d^2r/d\theta^2 = r - k, \quad (44)$$

with the solution

$$r - k = Ae^\theta + Be^{-\theta} = C \sinh \theta + D \cosh \theta. \quad (45)$$

Particular cases of these solutions (with A small and B zero or C small and D zero) represent closely wrapped

spirals very near to the circle $r = k$ (cf. Fig. 7). These solutions (i.e. those in which $dr/d\theta$ is small when r is close to k) are the only ones in which we obtain a spiral of many turns. However, k is less than $5b/\pi$ unless $b > 40\pi\gamma'/a\mu$, which is not far short of the requirement for the dislocation to have a hollow core.

The spiral may be continued by ruler-and-compass construction from the limit of validity of (45) (Figs. 6 and 7 were drawn in this way); and thereafter continued to infinity by (43). It is found to open out rapidly so that from $r = 1.1k$ it passes to infinity in less than one revolution of θ . Hence for the normal case of a dislocation with closed core there is a negligible surface depression of less than one molecular thickness in total depth. Only for border-line cases, in which b is nearly large enough to cause a hollow core, do we get a significant crater in the close-packed surface (represented by a spiral step line of many turns). This crater may be of any depth, in principle, but its radius is practically limited to the macroscopically small value k .

Note added 26 March 1951. At the time the above was written, the available observations which came nearest to the matter were those of Griffin (1950) on beryl, and discussion of this evidence, requiring detailed consideration of the interpretation of particular photographs, was left for later publication by Griffin himself.

In the interim further observations have become available. Dislocations of 15A. in six-layer hexagonal carborundum appear visibly hollow (A. R. Verma, private communication, to be published).

On the other hand, 47A. dislocations in long-chain paraffins (Dawson & Vand, 1951) are not hollow. The reason for this is clearly that the paraffin molecules can be longitudinally displaced to many alternative relative positions of only slightly higher energy than that of their proper position in the crystals. One way of describing this in the language of dislocations is that the complete dislocation is readily dissociated into a cluster of weak partial dislocations.

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