Interactions between cross-links and dislocations in polyethylene crystals: a model of irradiation hardening

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The irradiation hardening of polyethylene (PE) crystals is explained in terms of the intersection and interaction between cross-links and dislocations. The elastic energies and forces of interaction between cross-links and the dislocations responsible for the various plastic deformation modes are calculated using a force dipole model of a cross-link and the strain field of the dislocation. The elastic energies of interaction are in all cases less than 0.7 eV (1.12×10^{-19} J) and they are greater for edge than for screw dislocations. The hardening which arises from the direct intersections is calculated using a Morse potential model for the cross-link strength, and it is found that these interactions involve energies of the order of 3.6 eV (5.76×10^{-19} J). From these results it is concluded that at 0 K both types of interaction produce similar hardening. However, since the elastic interaction energies are small, the hardness of cross-linked PE crystals at moderate temperatures is due solely to direct intersections of cross-links and dislocations. The strongest interactions take place between cross-links and those dislocations which produce chain-axis slip and this explains why this mode of deformation is readily suppressed by irradiation. The forces of interaction between cross-links and twin dislocations are not negligible, but since their interaction energies are of the order of 0.1 eV (0.16×10^{-19} J), twinning deformation, at moderate temperatures, should not be affected by irradiation. By combining all the possible deformation modes, the relationship

$$\tau_c = 4\chi^{\frac{1}{2}},$$

is derived for the increase in yield stress, τ_c (GPa), in terms of the atomic concentration of cross-links, χ, provided that these are uniformly distributed in the crystal.

1. Introduction

The physical properties of polymers are greatly affected by ionizing radiation, and this effect has found important practical applications, for example, in the irradiation hardening of polyethylene. Since bulk deformation of polyethylene requires the plastic flow of the crystalline regions, the irradiation-induced changes in the crystalline phase should play a significant role in the hardening process.

Information about the effects of irradiation on the specific plastic deformation modes which operate within the polyethylene crystals is rather scarce. All results of importance have been obtained by Voigt-Martin [1] and Andrews and Voigt-Martin [2], and concern single crystals deposited from solution. Stress–strain curves for different densities of irradiated bulk polyethylene have also been obtained by these workers [3].

Both [0 0 1] (chain axis) slip and transverse slip systems are strongly suppressed by γ-irradiation doses from 10 to 160 Mrads. The operation of [1 1 0] twinning appears to be unaffected by irradiation, and there is some evidence to suggest that the orthorhombic to monoclinic phase transformation is inhibited [2].

The yield stress of bulk spherulitic material increases both with crystallinity and radiation

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dose and Andrews [3] has extrapolated the data to find that the yield stress of the crystalline phase increases by 10 MPa after a γ-irradiation dose of 160 Mrad.

Since cross-links between molecules are believed to be the main type of defect produced when polyethylene is exposed to ionizing radiation [5, 6], it seems justifiable to interpret the hardening effects in terms of interactions between the dislocations capable of producing plastic flow, and the cross-links which are formed both at the surface of the crystal lamellae and within the individual crystals.

The type of dislocations which can glide in polyethylene crystals are limited, and their properties have been discussed elsewhere by the present authors [6, 7]. Their interaction with cross-links is discussed in the present work using an elastic model of the cross-link [8, 9].

The glide dislocations which need to be considered here are those which, being energetically favourable, produce chain-axis slip, transverse slip, and twinning (Types 1, 3, 4, 6 and 7 of [6]).

2. Interactions between cross-links and dislocations

The type of interactions which can arise between cross-links and dislocations are illustrated in Figs 1 and 2. These show a projection of the crystal on to the (0 0 1) plane, with lines as cross-links between nearest-neighbour molecules. As a dislocation glides along the glide plane, R, it will experience a "direct" interaction with cross-links of Types 1 and 2, which intersect the glide plane. Further movement of the dislocation is possible

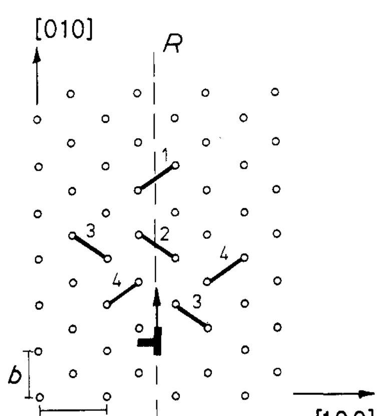

Figure 1 Projection of the (0 0 1)-plane showing the position of cross-linkes with respect to the (1 0 0) slip dislocation glide plane.

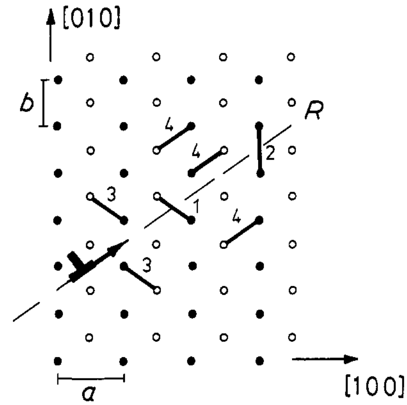

Figure 2 Projection of the (0 0 1)-plane showing the position of cross-links with respect to the (1 $\bar{1}$ 0) glide plane of a dislocation.

only by displacement, by the Burgers vector, of the two cross-linked molecules with respect to each other. In addition to the "direct" interaction, the cross-link has an associated stress field, so that as the dislocation glides, it will experience a varying "elastic force of interaction" with each cross-link in the crystal. Those cross-links which do not intersect the glide plane (Types 3 and 4) can only interact with the dislocation in this way ("elastic' interaction).

Both edge and screw dislocations can experience "direct" and "elastic" interactions in the way described above. Cross-links between first nearest neighbour molecules have been shown in Figs 1 and 2. These cross-links are parallel to [1 1 0], ([1 1 0]-type), or to [1 $\bar{1}$ 0] directions ([1 $\bar{1}$ 0]-type). Similar interactions would arise from cross-links between second nearest-neighbour molecules ([0 1 0]-type), one of which is shown in Fig. 2 (Type 2). As will become clear later, the interactions with first and second nearest-neighbour cross-links do not need to be considered separately.

3. Calculation of the elastic force of interaction

The elastic energy of interaction between a cross-link and a dislocation can be calculated using the continuum strain model of the cross-link obtained previously by the present authors [8, 9]. In this model the cross-link is described by a set of three orthogonal force dipoles, or by the force dipole tensor, p_{ij}, with principal components

$$p_{11} = -(5.38 \pm 0.04) \times 10^{-19}\ \text{J},$$

$$p_{22} = (6.03 \pm 2.54) \times 10^{-20}\ \text{J}$$

and

$$p_{33} = -(34.0 \pm 0.11) \times 10^{-19}\ \mathrm{J}.$$

The linear elastic energy of interaction is given by [10].

$$E_{\text{int}} = -p_{ij}\epsilon_{ij}^{\mathrm{D}}, \tag{1}$$

where p_{ij} are the force dipole moments representing the cross-link and $\epsilon_{ij}^{\mathrm{D}}$ are components of the dislocation strain field at the cross-link.

In a co-ordinate system, ξ_i', with axes parallel to the directions of principal strains of the cross-link (as shown in Fig. 3) Equation 1 takes the form:

$$E_{\text{int}} = -(p_{11}\epsilon_{11}^{\mathrm{D}'} + p_{22}\epsilon_{22}^{\mathrm{D}'} + p_{33}\epsilon_{33}^{\mathrm{D}'}). \tag{2}$$

The dislocation strains can be written (for orthorhombic symmetry) in terms of the dislocation stresses, σ_{ij}^{D},

$$\epsilon_{11}^{\mathrm{D}} = S_{11}\,\sigma_{11}^{\mathrm{D}} + S_{12}\,\sigma_{22}^{\mathrm{D}} + S_{13}\,\sigma_{33}^{\mathrm{D}}; \tag{3}$$

$$\epsilon_{22}^{\mathrm{D}} = S_{21}\,\sigma_{11}^{\mathrm{D}} + S_{22}\,\sigma_{22}^{\mathrm{D}} + S_{23}\,\sigma_{33}^{\mathrm{D}}; \tag{4}$$

$$\epsilon_{33}^{\mathrm{D}} = S_{31}\,\sigma_{11}^{\mathrm{D}} + S_{32}\,\sigma_{22}^{\mathrm{D}} + S_{33}\,\sigma_{33}^{\mathrm{D}}; \text{ and} \tag{5}$$

$$\epsilon_{12}^{\mathrm{D}} = \frac{S_{66}\,\sigma_{12}^{\mathrm{D}}}{2}, \tag{6}$$

where S_{ij} are the elastic constants as given in the Appendix. The stress fields of infinitely-long straight dislocations lying parallel to diad axes have been obtained elsewhere [11] by standard methods [12, 13] and are also given in the Appendix.

It is necessary to transform the strains, $\epsilon_{ij}^{\mathrm{D}}$, (in the ξ_i system) into the $\epsilon_{11}^{\mathrm{D}'}$ (referred to the ξ_i' system) which are to be used in Equation 2,

$$\epsilon_{11}^{\mathrm{D}'} = \epsilon_{11}^{\mathrm{D}}\cos^2\alpha + \epsilon_{22}^{\mathrm{D}}\sin^2\alpha + 2\epsilon_{12}^{\mathrm{D}}\sin\alpha\cos\alpha, \tag{7}$$

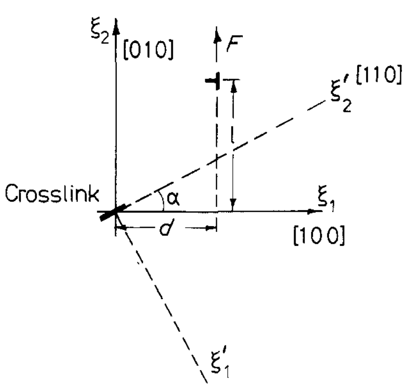

Figure 3 Co-ordinate systems used in the calculation of the force of interaction.

$$\epsilon_{22}^{\mathrm{D}'} = \epsilon_{11}^{\mathrm{D}}\sin^2\alpha + \epsilon_{22}^{\mathrm{D}}\cos^2\alpha - 2\epsilon_{12}^{\mathrm{D}}\sin\alpha\cos\alpha, \tag{8}$$

$$\epsilon_{33}^{\mathrm{D}'} = \epsilon_{33}^{\mathrm{D}}. \tag{9}$$

The energy of interaction given by Equation 2 is obviously a function of the co-ordinates of the cross-link with respect to the dislocation. The relative position of the dislocation with respect to the cross-link can be described by the parameters d (perpendicular distance from the cross-link to the slip plane of the dislocation), and l (distance between cross-link and dislocation projected on to the slip plane).

The glide force of interaction, or the force exerted by the cross-link on the dislocation, resolved in the glide direction, is simply given by

$$F_{\text{glide}} \equiv F = -\left(\frac{\partial E_{\text{int}}}{\partial l}\right)_d. \tag{10}$$

This force has been calculated for several types of dislocations and for the orientations of interest. The results are presented in Figs 4 and 6 to 8.

3.1. Edge dislocation of ⟨0, *b*, 0⟩ Burgers vector lying along [0 0 1] (Type 6)

As shown in Fig. 4, the glide plane of this dislocation is (1 0 0). A [1 1 0]-type cross-link is also shown in Fig. 4.

When the glide plane intersects the cross-link, i.e. $d = 0$, the glide force, F, is given by

$$F = 0.1\frac{p_{11}b}{l^2}, \tag{11}$$

where b is the magnitude of the dislocation Burgers vector. At the cross-link itself ($l = 0$) where the elastic force of interaction cannot be estimated, the "direct" interactions are more important. These interactions will be discussed later.

For any other glide plane ($d \neq 0$) the glide force is that plotted in Fig. 4. For a cross-link of the $[1\bar{1}0]$-type the force–distance curve would be a reflection of that shown in Fig. 4 in both axes.

In this result it is noted that the cross-link acts as a short-range obstacle to the dislocation motion with both attractive and repulsive forces which have about the same maximum value, $F_{\max}$, where $F_{\max}$, where

$$F_{\max} \simeq |0.1p_{11}b/d^2|. \tag{12}$$

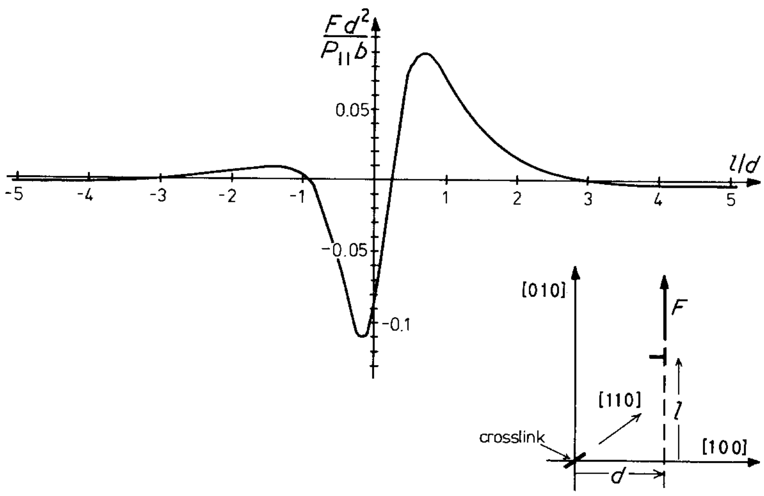

Figure 4 Force of interaction between a [110] cross-link and a [0, b, 0] edge dislocation gliding on a (100) plane.

The cross-links which interact most strongly with the dislocation are those adjacent to the glide plane, for which $d = a/2 = 3.7 \times 10^{-10}$ m, where a is the unit cell parameter. This gives $F \simeq 2 \times 10^{-10}$ N for the maximum interaction force.

The difference between the maximum and minimum energies of interaction (corresponding to the positions where $F = 0$) is found to be $\Delta E \simeq 0.44$ eV, (7.1×10^{-20} J), and this small value suggests that dislocations can easily overcome the obstacle offered by the cross-link with the help of thermal fluctuations.

An initially straight dislocation moving under the action of an applied stress will bow-out between the cross-link obstacles, as shown in Fig. 5. The dislocation will overcome the cross-link at a critical angle θ given by

$$F_{\max} \simeq 2T(\theta)\sin\theta \tag{13}$$

where $T(\theta)$ is the dislocation line tension. If $F_{\max}$ is so large that the equality is never satisfied, not even for $\theta = 90°$, the dislocation bypasses the cross-link by the Orowan mechanism [14].

Values of $T(\theta)$ for all dislocation types which

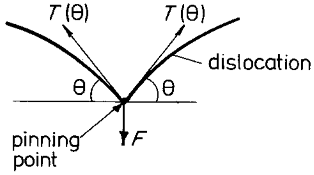

Figure 5 Bowing out of a dislocation segment around a pinning point.

are of interest here have been obtained and published elsewhere [7]. Taking $F_{\max} \simeq 2 \times 10^{-10}$ N and the value of $T(\theta)$ from Fig. 4 of [7] the breakaway condition is obtained,

$$\sin\theta = \frac{10^{-10}}{T}, \tag{14}$$

where T is the line tension in N.

Comparison of this condition with Fig. 4 of [7] shows that the breakaway angle is $\theta \simeq 22°$, so that the dislocation does not need to bow far from the pure edge orientation to overcome such cross-links.

The stress, τ_c, needed to drive this Type 6 dislocation through a random distribution of cross-links, excluding the "direct" interations, can be estimated using the Friedel relation [15] *.

$$\tau_c = \frac{2n^{\frac{1}{2}}}{bT^{\frac{1}{2}}}\left(\frac{F_{\max}}{2}\right)^{\frac{3}{2}}, \tag{15}$$

where n is the area density of cross-links of strength $F_{\max}$ on the glide plane. With $T \simeq 2.8 \times 10^{-10}$ N this stress becomes $\tau_c \simeq 0.242 n^{1/2}$ N m^{-1}. This can be written in terms of the atomic concentration of cross-links of any type, χ, as in [11], $\tau_c \simeq 1.4\chi^{1/2}$ GPa. This is an estimate of the hardening produced by the "elastic" interactions at 0 K, in the absence of thermal fluctuations. As pointed out before, the energy required to overcome the interaction is only $\Delta E \simeq 0.44$ eV (7.1×10^{-20} J), and this is reduced to 0.1 eV (1.6×10^{-20} J) at a stress of about half of the athermal stress, τ_c. Therefore, thermally-aided motion can occur easily at room

*It may be worthwhile to point out that the $F_{\max}$ in Equation 15 is a localized resistance force which is taken here to be the same as the $F_{\max}$ obtained by the method of Section 3.

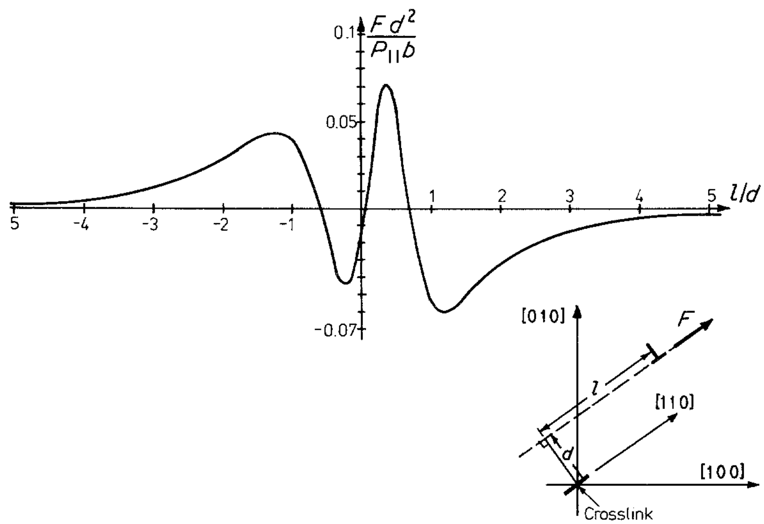

Figure 6 Force of interaction between a [1 1 0] cross-link and a $\eta[a, b, 0]$ edge dislocation gliding on a $(1\bar{1}0)$ plane.

temperature and the hardening effect of this type of interaction is probably negligible at this temperature.

3.2. Edge dislocation of $\eta\langle a, b, 0\rangle$ Burgers vector lying along [0 0 1], (Type 7)

The perfect dislocation, where $\eta = 1$, if it exists at all, is most probably dissociated into partials [6] so that the partial dislocations where $\eta = 0.5$, 0.386 and 0.114 will be considered here. The first of these is a slip dislocation, the other two are the ⟨1 1 0⟩ complementary twin, and the ⟨1 1 0⟩ twin partial dislocations, respectively. These dislocations glide on the $(1\bar{1}0)$ plane and interact with [1 1 0] cross-links, as shown in Fig. 6.

The glide force of interaction when $d = 0$ is given by

$$F = -0.068 p_{11} b/l^2 \qquad (16)$$

and for any other value of d, ($d \neq 0$) the glide force is represented graphically in Fig. 6. This force is attractive on one side of the cross-link, and repulsive on the other, the maximum values of F_{max} being of about the same magnitude, i.e.,

$$F_{max} \simeq |0.06 p_{11} b/d^2|. \qquad (17)$$

The strongest interaction is experienced with cross-links which are at a distance of one interatomic spacing from the glide plane, ($d = 2.1 \times 10^{-10}$ m), and with $\mathbf{b} = \eta(a^2 + b^2)^{1/2}$, the maximum values of this force, F_m, for the three different dislocations Burgers vectors are given in Table I where the critical angles, θ, the critical stresses, τ_c, and the interaction energies, ΔE, are also tabulated.

In obtaining the values in Table I, the line tension, T, has been estimated from the data of Figs 4 and 6 of [7], and the nearly-hexagonal nature of the polyethylene lattice has been invoked. In the calculation of τ_c in terms of the atomic concentration of cross-links, χ, the fact that only half of the total number of nearest-neighbour cross-links are of the [1 1 0]-type has also been taken into account.

The result, that the angle, θ, for the 0.114 ⟨a, b, 0⟩ twin dislocation is $> 90°$, implies that these dislocations must by-pass the cross-links by the Orowan looping mechanism, in which case the critical stress, τ_c, is given by [14]

$$\tau_c = 2Tn^{\frac{1}{2}}/b. \qquad (18)$$

The values of ΔE are all low enough, especially for the twin partial dislocation, for thermally-aided motion past the obstacles to be easy at room temperature.

TABLE I Data for the elastic interaction between $\eta\langle a, b, 0\rangle$ dislocations and [1 1 0]-type cross-links

Dislocation with $\mathbf{b} \equiv \eta\langle a, b, 0\rangle$	F_{max}($\times 10^{-10}$ N)	θ(°)	$\tau_c n^{-1/2}$ (Nm^{-1})	$\tau_c \chi^{-1/2}$ (GPa)	ΔE (eV)
$\eta = \frac{1}{2}$	3.2	40–65	0.58	2.4	0.7
$\eta = 0.386$	3.0	40–65	0.68	2.8	0.54
$\eta = 0.114$	0.73	> 90	0.31	1.3	0.16

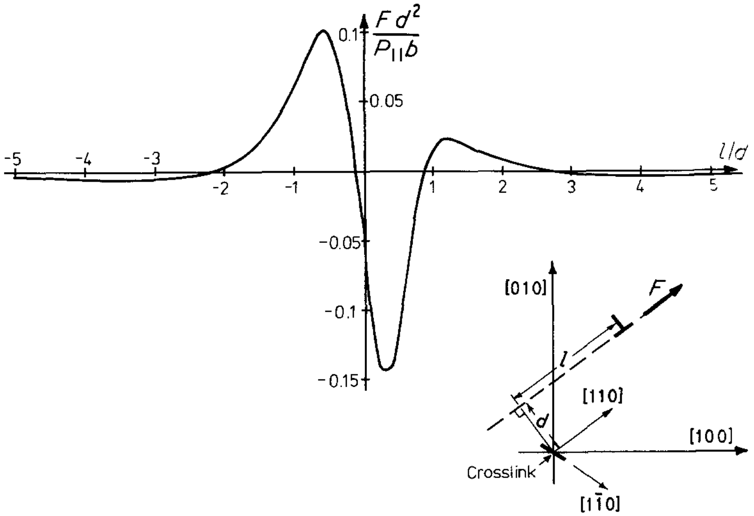

Figure 7 Force of interaction between a [1$\bar{1}$0] cross-link and a $\eta[a, b, 0]$ edge dislocation gliding on a (1$\bar{1}$0) plane.

The elastic force of interaction between Type 7 dislocations and cross-links of [1$\bar{1}$0]-type (configuration of Fig. 7) is plotted in Fig. 7 for any value of $d \neq 0$. The maximum value of this force is approximately

$$F_{\max} \simeq |0.12p_{11}b/d^2|. \quad (19)$$

Using again the data of Figs 4 and 6 of [7], and the appropriate values of b, the set of values of Table II are obtained for the athermal stresses and energies required to drive the dislocations through a random concentration of [1$\bar{1}$0] cross-links not intersecting the slip plane. From the values of ΔE it is clear the thermally-activated motion will be easy at moderate temperatures, in particular at room temperature.

3.3. Screw dislocations with $\langle 0, b, 0\rangle$ Burgers vector (Type 3)

This dislocation produces transverse slip and glides on the [100] plane. Its interaction with a [110] cross-link is illustrated by the configuration of Fig. 8. When $d = 0$ the interaction force is

$$F = 0.0726p_{11}b/l^2, \quad (20)$$

and this is the same, but of opposite sign, if the cross-link is in the [1$\bar{1}$0]-direction. For any other slip plane ($d \neq 0$) the interaction force with a [110] cross-link is as plotted in Fig. 8. Again, for a [1$\bar{1}$0] cross-link the interaction is the same but of opposite sign. The maximum value of F in Fig. 8 is about $|0.055p_{11}b/d^2|$, and the minimum is of opposite sign but only of magnitude $|0.007p_{11}b/d^2|$. Therefore, the strength of the elastic obstacle that the cross-link presents to the $\langle 0, b, 0\rangle$ screw dislocation depends upon the direction in which the dislocation is moving.

Considering only the strongest interaction, for which $F_{\max} \simeq 10^{-10}$ N, the critical breaking angle for a bowing dislocation is given by

$$\sin\theta = \frac{0.41 \times 10^{-10}}{T}, \quad (21)$$

and from Fig. 4 of [7] this is found to be $\theta \simeq 5°$. The dislocation remains almost straight as it overcomes the cross-link. Taking $T \simeq 5.6 \times 10^{-10}$ N [9], the athermal critical stress becomes $\tau_c \simeq 0.06n^{1/2}$ N m^{-1} $= 0.24\chi^{1/2}$ GPa. This is clearly much smaller than the critical stress arising from the interaction with edge dislocations of the same Burgers vector. Furthermore, the energy required to drive the dislocation past the obstacle is $\Delta E = 0.06p_{11}b/d$, or $\Delta E = 0.27$ eV (0.43×10^{-19} J) for the strongest cross-links, so that these cross-links present a very weak obstacle to the motion of $\langle 0, b, 0\rangle$ screw dislocations at room temperature.

TABLE II Data for the elastic interaction between $\eta\,\langle a, b, 0\rangle$ dislocations and [1$\bar{1}$0] type cross-links

Dislocation with $\mathbf{b} \equiv \eta\,\langle a, b, 0\rangle$	$F_{\max}$($\times 10^{-10}$ N)	θ(°)	$\tau_c n^{-1/2}$ (Nm^{-1})	$\tau_c \chi^{-1/2}$ (GPa)	ΔE (eV)
$\eta = \frac{1}{2}$	1.7	23–59	0.23	1.0	0.36
$\eta = 0.386$	2.0	23–59	0.27	1.2	0.28
$\eta = 0.114$		74	0.31	1.3	0.08

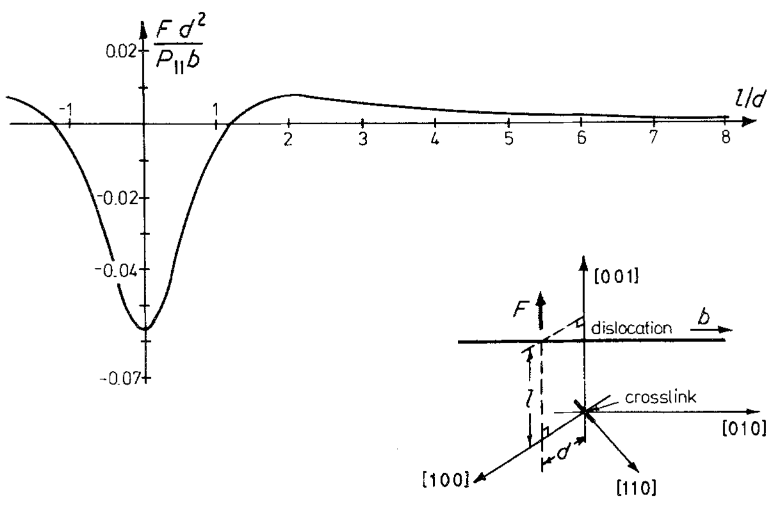

Figure 8 Force of interaction between a [1 1 0] cross-link and a [0, *b*, 0] screw dislocation gliding on a (1 0 0) plane.

3.4. Screw dislocations with $\eta \langle a, b, 0\rangle$ Burgers vector, (Type 4)

The stress field of this dislocation which glides on the (1 1 0)-plane, producing transverse slip, has not been obtained explicitly, but the interaction with cross-links can be estimated by invoking the nearly-hexagonal symmetry of the polyethylene lattice. It is to be noted that in this approximation there is no elastic interaction between the dislocation and a cross-link which is parallel to it (as for the dotted cross-link shown in Fig. 9). After taking the difference in Burgers vector and interplanar spacing into account, the results of Fig. 8 can be used to estimate the interaction between the dislocation and "oblique" (or non-parallel) cross-links. This force depends also upon the direction of movement of the dislocation. It has a maximum value of $1.5 \times 10^{-10}\ \eta$ N, when the dislocation moves in the [0 0 1]-direction in Fig. 9, and a maximum value of $2 \times 10^{-11}\ \eta$ N, when the dislocation moves in the opposite direction. Using the data of Figs 4 and 6 of [7], and the largest interaction force, it is estimated that the critical breaking angle for the $\frac{1}{2}\langle a, b, 0\rangle$ and 0.386 $\langle a, b, 0\rangle$ partial dislocations is less than 12°. The twin partial 0.114 $\langle a, b, 0\rangle$, which must move in the [0 0 1]-direction to produce the twin monolayer, experiences a much smaller interaction force, of only 2.3×10^{-12} N, with a critical breaking angle $\theta < 6°$. The cross-links present are therefore very weak obstacles to the $\eta\langle a, b, 0\rangle$ screw dislocations at 0 K. With the aid of thermal fluctuations the strength of the obstacles would be negligible at room temperature.

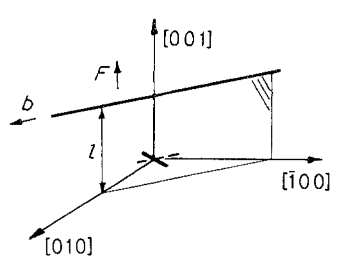

Figure 9 $\eta[a, b, 0]$ screw dislocation gliding on a $(1\bar{1}0)$ plane.

3.5. Screw dislocations with [0, 0, *c*] Burgers vector, (Type 1)

This is the only dislocation which can produce chain-axis slip and it has no linear elastic interaction with cross-links lying on [0 0 1]-planes because, for this dislocation,

$$\epsilon_{11}^{D'} = \epsilon_{22}^{D'} = \epsilon_{33}^{D'} = 0. \qquad (22)$$

A small non-linear long-range interaction can arise, since the dislocation will produce a small shear of the cross-linked molecules along their length, changing the cross-link orientation, but this is a minor effect when compared with the interaction which arises from the direct intersection, to be discussed later.

4. Direct interaction between cross-links and dislocations

The "direct" interactions arise when the cross-links intersect the glide plane of the dislocations, as in the case of cross-links of Types 1 and 2 of Figs 1 and 2. The direct interaction with a cross-link of Orientation 1 should be relatively weak because, if the dislocation overcomes the elastic force and glides past the cross-link, this is only re-orientated from Position 1 to Position 2. The elastic energy of the cross-link is not increased, and it is unlikely that the cross-link will be broken provided that chain rotation can occur. The force needed for such a re-orientation cannot be readily estimated but it seems reasonable to assume that it will not be greater than the maximum force of interaction which, at $l \simeq 4 \times 10^{-10}$ m is about 1.6×10^{-10} N. It has already been shown above that an obstacle of this strength is weak, especially at temperatures other than 0 K. After the passage of dislocations, all the cross-links of Type 1 will be re-orientated to Position 2 and in this orientation they will interact more strongly with further intersecting dislocations of the same type. Even if the elastic force of interaction at small separations is overcome, the dislocation can cut through the cross-link of Type 2 only if this is stretched or broken. In order to investigate the possibility of either of these two processes occurring, the energy and force required to break a C–C bond must be calculated.

4.1. The strength of a C–C bond

The potential energy, U, of a covalent bond in terms of the interatomic separation, r, can be expressed by the Morse potential [16]

$$U(r) = D[1 - e^{-a(r-r_e)}]^2, \qquad (23)$$

where D is the dissociation energy, r_e is the equilibrium separation of the atoms, and a is a constant. The force acting on each carbon atom towards the other is

$$F(r) = dU/dr = 2aD\{\exp[-a(r-r_e)] - \exp[-2a(r-r_e]\}, \qquad (24)$$

and it has a maximum value

$$F(r') = aD/2, \qquad (25)$$

where

$$r' = r_e + \frac{\ln 2}{a}. \qquad (26)$$

The value of D for a C–C bond in a chain hydrocarbon is given as $D \simeq 3.6$ eV (5.76×10^{-19} J) while for the diatomic molecule it is $D \simeq 5.6$ eV (8.96×10^{-19} J) [17]. The value of a can be obtained from the first force constant, f, in the potential function, U', for the simple harmonic oscillator,

$$U' = \tfrac{1}{2} f x^2, \qquad (27)$$

where $x \equiv r - r_e$. This can be equated to

$$U' = Da^2x^2, \qquad (28)$$

obtained from Equation 23 for small values of x, to give:

$$f = 2Da^2. \qquad (29)$$

Values of f for both the C–C diatomic molecule and the C–C bond in large molecules are given as 9.25×10^2 N m^{-1} and 4.5×10^2 N m^{-1}, respectively [18]. Moelwyn-Hughes [19] quotes values of $f = 9.466 \times 10^2$ N m^{-1} and 5×10^2 N m^{-1} for the C–C molecule and the ethane molecule, respectively. It seems then reasonable to accept the values $D = 3.60$ eV and $f = 4.5 \times 10^2$ N m^{-1} for the C–C bond in polyethylene, which give $a = (f/2D)^{1/2} = 1.98 \times 10^{10}$ m^{-1}. The strength of the bond, or force needed to break the bond, is, from Equation 24. $F = 5.7 \times 10^{-9}$ N and the atomic separation at which the bond breaks is (with $r_e = 1.54 \times 10^{-10}$ m) $r' = 1.89 \times 10^{-10}$ m. The breaking strain of the cross-link is therefore 0.23.

4.2. Direct interaction with "transverse slip" dislocations

The force required to break the cross-link is much greater than the largest force which can arise from elastic interactions and it cannot be provided by any dislocation with $\langle 0, b, 0 \rangle$ Burgers vector bowing-out with an angle $\theta < 90°$. The energy needed to break the cross-link is 3.6 eV, and this is too high for thermal fluctuations to make any significant contribution to the breaking process.

The direct interaction must therefore be overcome by Orowan looping or by bond stretching. Since the maximum stretch possible without breaking the cross-link is 23%, the cross-linked molecules would have to suffer a displacement nearly equal to a $\frac{1}{2}\langle a, b, 0 \rangle$ lattice vector. The self-energy of the cross-link would be so high, and its elastic interaction with the dislocation so large, that by-passing by Orowan looping would probably occur under a much smaller stress. This stress is, again, given by Equation 18 in terms of the cross-link density, n. With values for the line tension taken from Fig. 4 of [7] this stress becomes $\tau_c = 1.5 n^{1/2}$ N m^{-1} $= 4.2\chi^{1/2}$ GPa for both $\langle 0, b, 0 \rangle$ edge and $\langle 0, b, 0 \rangle$ screw dislocations (Types 3 and 6).

A similar consideration of the direct interaction of $\eta\langle a, b, 0 \rangle$ dislocations with cross-links shows that the passage of a $\frac{1}{2}\langle a, b, 0\rangle$ and/or a 0.386 $\langle a, b, 0\rangle$ partial is easy when the cross-link is re-oriented without being greatly stretched (Fig. 2). When the cross-links have been re-oriented so that they join second-nearest-neighbour molecules, the movement of further dislocations in the same glide plane is strongly inhibited. Thus, multiple slip by the movement of $\langle a, b, 0\rangle$ dislocations as a dissociated pair would have to take place by the Orowan mechanism under a stress which is estimated to be, (assuming hexagonal symmetry) $\tau_c \simeq 1.35n^{1/2}$ N m^{-1} = $4\chi^{1/2}$ GPa.

Of particular interest is the case of a 0.114 $\langle a, b, 0\rangle$ edge partial which, in order to produce the twin monolayer, must glide in the [1 1 0]-direction. The direct intersection can be achieved by a small rotation of the cross-link, so that only the elastic force of interaction ($F_{max} = 2.3 \times 10^{-11}$ N, at $l = 4 \times 10^{-10}$ m is significant. This force is overcome when the dislocation bows-out to an angle $\theta \simeq 60°$. A similar conclusion is reached for the 0.114 $\langle a, b, 0\rangle$ twin screw dislocation which glides in the [0 0 1]-direction to produce the twin monolayer. The stress needed to overcome the cross-links is not negligible, ($\tau_c \simeq 0.308n^{1/2}$ N m^{-1} = $0.9\chi^{1/2}$ GPa) but the interaction energy is small and the critical stress, τ_c, would be greatly reduced by thermal activation at room temperature.

4.3. Interaction with the $\langle 0, 0, c\rangle$ chain-slip dislocation

A $\langle 0, 0, c\rangle$ screw dislocation should, in principle, be able to glide on any plane of the [0 0 1] zone, and this apparent ability to escape from any defect obstructing its motion seems to contradict the experimental evidence for suppression of c-axis slip by irradiation. It should be noted, however, that the slip plane of these dislocations is largely restricted by the orientation of the surface folds, and intersection with cross-links should readily occur because, as the dislocation moves, there is no linear elastic interaction force before a direct intersection takes place. Such an intersection is unlikely to break the C–C cross-link bond. This is because, although the line tension of the $\langle 0, 0, c\rangle$ screw dislocation is very high, it decreases rapidly to zero as it deviates from this orientation by only 15° (Fig. 7 of [7]) and the dislocation cannot exert a large force on the pinning point.

This large anisotropy of the dislocation line tension makes it extremely difficult for the dislocation to overcome the cross-links by Orowan looping. For this to happen dislocation loops with edge segments would have to be left around the cross-links, as shown in Fig. 10. The energy of the edge segments, and that of the dislocation configuration of Fig. 10 is very high and could only be achieved by a very large external stress. Unfortunately it is difficult to make a quantitative estimate of this stress because this dislocation will always tend to maximize the length of its screw component and its bowing cannot be treated as that of a flexible string with nearly constant line tension.

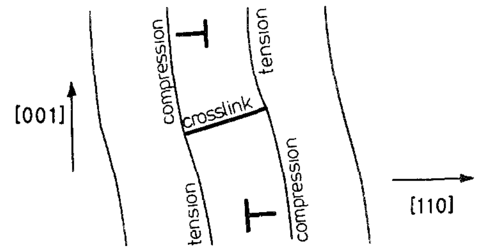

Figure 10 The edge segment of a [0, 0, c] dislocation loop around a cross-link producing bending of the molecular chains.

If the dislocations were to cut through the cross-link without breaking it, the configuration of the defect which would be left behind would be as shown schematically in Fig. 11. The C–C bond at the cross-link would join atoms on different (0 0 1) planes. Large molecular bending and stretching with considerable lattice distortion would be required, hence this mode of intersection leaves a configuration very similar to that produced by Orowan looping, and it should require about the same stress. The cross-links existing at the surface folds of the crystals would probably be easier to cut.

5. Discussion and conclusions

The deformation modes which produce transverse

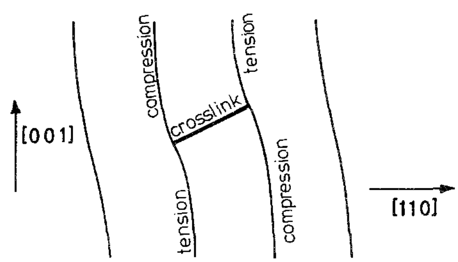

Figure 11 Bending of the molecular chains resulting from the stretching of the cross-link along [0 0 1].

slip in polyethylene crystals are made more difficult as a result of both "elastic" and "direct" interactions between cross-links and dislocations with $\langle 0, b, 0\rangle$ and $\frac{1}{2}\langle a, b, 0\rangle$ Burgers vectors (Types 3, 4, 6 and 7). Since the screw dislocations are able to overcome elastic interactions at a much lower stress than the corresponding edges, the latter only need to be taken into account in any discussion of the hardening arising from such interactions.

All the elastic interactions which can arise in the deformation by transverse slip produce a hardening, or increase in yield stress at 0 K, which is between $1.4\chi^{1/2}$ GPa and $3.4\chi^{1/2}$ GPa where χ is the number of cross-links per carbon atom in the crystal.

The contribution to the hardening which arises from the "direct" interactions, in transverse slip, results in an increase of the yield stress of about $4\chi^{1/2}$ GPa at 0 K, so that the hardening is not much greater than that due to elastic interactions.

Whilst at very low temperatures both types of interaction make nearly-equal contributions to the hardening, the situation is very different at higher temperatures. The energy needed to overcome elastic interactions is only a fraction of 1 eV, and thermal fluctuations can help to reduce the hardening to a negligible level above the glass-transition temperature of polyethylene. However, the hardening arising from direct interactions should persist possibly up to the melting temperature of polyethylene because thermal activation would only make an insignificant contribution to the energy needed to overcome these interactions, which is about 3.6 eV.

Since the re-orientation of a cross-link without stretching requires only a small energy, a limited amount of transverse slip may occur at a lower stress by the thermally-aided "unit slip" of $\frac{1}{2}\langle a, b, 0\rangle$ dislocations. This seems to have been observed in the deformation of irradiated polyethylene crystals, even when all other slip modes had been entirely suppressed [2].

Transverse $\langle 1\,1\,0\rangle$ twinning as a deformation mode should become more difficult at 0 K as a result of both elastic and direct interactions between 0.114 $\langle 1\,1\,0\rangle$ dislocations and cross-links. Both types of interaction raise the twinning stress by about the same amount: between 1 and $2\chi^{1/2}$ GPa. However, at temperatures above the glass-transition temperature the twinning dislocations should be able to overcome easily any interaction with cross-links with the aid of thermal activation. This could explain why twinning is observed to operate more easily than slip at room temperature in irradiated crystals [2].

Qualitative arguments have been presented above to suggest that the c-chain axis slip, due to glide of $\langle 0, 0, c\rangle$ screw dislocations, is made very difficult by the direct dislocation–cross-link interactions. In fact the stress which would be required for rigid screw dislocations to break through a concentration, χ, of cross-links could be 100 times greater than that needed to activate transverse slip under the same cross-link concentration [11]. Of course such a large stress may not even be attainable, as is suggested by the results of Voigt-Martin and Andrews [2] who observed micro-cracking of the irradiated crystals before any evidence for any c-chain axis slip could be detected.

Any plasticity after irradiation seems to be due to the movement of dislocations producing transverse slip and, if this is the case, the degree of hardening or increase in yield stress produced by interaction with cross-links is expected to be of the order of $4\chi^{1/2}$ GPa. There is not much experimental data with which to compare this, but Andrews [3] has calculated that 160 Mrads of γ-radiation gives a crystallite hardening of about 10 MPa and therefore this gives $\chi = 6.25 \times 10^{-6}$ for the cross-link concentration. This represents one cross-link per 160 000 carbon atoms, or an average cross-link spacing of 1.6×10^{-8} m, which is not unreasonable, since it is of the same order of magnitude as the crystallite thickness.

Appendix

The elastic constants S_{ij} are given in terms of the stiffnesses C_{ij} as,

$$S_{11} = (C_{22}C_{33} - C_{23}^2)/\Gamma$$

$$S_{22} = (C_{11}C_{33} - C_{31}^2)/\Gamma$$

$$S_{33} = (C_{11}C_{22} - C_{12}^2)/\Gamma$$

$$S_{44} = 1/C_{44}$$

$$S_{55} = 1/C_{55}$$

$$S_{66} = 1/C_{66}$$

$$S_{12} = (C_{31}C_{23} - C_{12}C_{33})/\Gamma$$

$$S_{23} = (C_{12}C_{31} - C_{23}C_{11})/\Gamma$$

TABLE AI Dislocations parallel to [100] (where $\beta = 1$ GPa)

$$\frac{\sigma_{11}}{\beta} = \frac{b_2x_3(-0.298\,x_2^2 + 0.00421\,x_3^2) + b_3x_2(0.124\,x_2^2 + 0.0723\,x_3^2)}{(x_2^4 + 2.99\,x_2^2\,x_3^2 + 0.034\,x_3^4)}$$

$$\frac{\sigma_{22}}{\beta} = \frac{-b_2x_3(2.362\,x_2^2 + 0.0253\,x_3^2) + b_3x_2(0.745\,x_2^2 - 0.137\,x_3^2)}{(x_2^4 + 2.99\,x_2^2\,x_3^2 + 0.034\,x_3^4)}$$

$$\frac{\sigma_{33}}{\beta} = \frac{b_2x_3(0.745\,x_2^2 - 0.137\,x_3^2) + b_3x_2(4.05\,x_2^2 + 12.84\,x_3^2)}{(x_2^4 + 2.99\,x_2^2\,x_3^2 + 0.034\,x_3^4)}$$

$$\frac{\sigma_{12}}{\beta} = \frac{-0.533\,b_1x_3}{(x_2^2 + 2.64\,x_3^2)}$$

$$\frac{\sigma_{23}}{\beta} = \frac{(b_2x_2 + b_3x_3)(0.745\,x_2^2 - 0.137\,x_3^2)}{(x_2^4 + 2.99\,x_2^2\,x_3^2 + 0.034\,x_3^4)}$$

$$\frac{\sigma_{31}}{\beta} = \frac{0.202\,b_1x_2}{(x_2^2 + 2.64\,x_3^2)}$$

TABLE AII Dislocations parallel to [010] (where $\beta = 1$ GPa)

$$\frac{\sigma_{11}}{\beta} = \frac{b_3x_1(2.20\,x_3^2 - 16.07\,x_1^2) + b_1x_3(0.302\,x_3^2 + 100.9\,x_1^2)}{(x_3^4 + 326.8\,x_3^2\,x_1^2 + 53.2\,x_1^4)}$$

$$\frac{\sigma_{22}}{\beta} = \frac{b_3x_1(-14.54\,x_3^2 - 6.08\,x_1^2) + b_1x_3(0.114\,x_3^2 + 22.82\,x_1^2)}{(x_3^4 + 326.8\,x_3^2\,x_1^2 + 53.2\,x_1^4)}$$

$$\frac{\sigma_{33}}{\beta} = \frac{-b_3x_1(735.9\,x_3^2 + 117.2\,x_1^2) + b_1x_3(2.20\,x_3^2 - 16.07\,x_1^2)}{(x_3^4 + 326.8\,x_3^2\,x_1^2 + 53.2\,x_1^4)}$$

$$\frac{\sigma_{12}}{\beta} = \frac{0.384\,b_2x_3}{(x_3^2 + 1.37\,x_1^2)}$$

$$\frac{\sigma_{23}}{\beta} = \frac{-0.528\,b_2x_1}{(x_3^2 + 1.37\,x_1^2)}$$

$$\frac{\sigma_{31}}{\beta} = \frac{(b_3x_3 + b_1x_1)(2.20\,x_3^2 - 16.07\,x_1^2)}{(x_3^4 + 326.8\,x_3^2\,x_1^2 + 53.2\,x_1^4)}$$

TABLE AIII Dislocations parallel to [001] (where $\beta = 1$ GPa)

$$\frac{\sigma_{11}}{\beta} = \frac{-b_1x_2(1.094\,x_1^2 + 0.221\,x_2^2) + b_2x_1\,(0.398\,x_1^2 - 0.297\,x_2^2)}{(x_1^4 + 2.003\,x_1^2\,x_2^2 + 0.555\,x_2^4)}$$

$$\frac{\sigma_{22}}{\beta} = \frac{b_1x_2(0.398\,x_1^2 - 0.297\,x_2^2) + b_2x_1(0.535\,x_1^2 + 147\,x_2^2)}{(x_1^4 + 2.003\,x_1^2\,x_2^2 + 0.555\,x_2^4)}$$

$$\frac{\sigma_{33}}{\beta} = \frac{b_1x_2(-0.168\,x_1^2 - 0.267\,x_2^2) + b_2x_1(0.483\,x_1^2 + 0.799\,x_2^2)}{(x_1^4 + 2.003\,x_1^2\,x_2^2 + 0.555\,x_2^4)}$$

$$\frac{\sigma_{12}}{\beta} = \frac{(b_1x_1 + b_2x_2)(0.398\,x_1^2 - 0.297\,x_2^2)}{(x_1^4 + 2.003\,x_1^2\,x_2^2 + 0.555\,x_2^4)}$$

$$\frac{\sigma_{23}}{\beta} = \frac{0.273\,b_3x_1}{(x_1^2 + 0.276\,x_2^2)}$$

$$\frac{\sigma_{31}}{\beta} = \frac{-0.0652\,b_3x_2}{(x_1^2 + 0.276\,x_2^2)}$$

and

$$S_{31} = (C_{23}C_{12} - C_{31}C_{22})/\Gamma,$$

where

$$\Gamma = C_{11}C_{22}C_{33} - C_{11}C_{23}^2 - C_{22}C_{31}^2 - C_{33}C_{12}^2 + 2C_{12}C_{23}C_{31} > 0.$$

The values of C_{ij} used in this paper have been taken from [6].

With these values, the stress fields of infinitely-long straight dislocations are given by the following expressions when referred to a co-ordinate system with axes parallel to the unit cell vectors [11].

The stress fields for dislocations parallel to [100], [010] and [001] are given in Tables AI to AIII, respectively.

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