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Radiation damage of polyethylene single crystals in electron microscopy between 1 and 2.5 MV. II. The influence of temperature

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Abstract. — The critical dose measured for polyethylene single crystals at 2 MV is increased by a factor of 4 between 300 K and 20 K. Below 100 K the intermediate hexagonal crystalline phase was not observed. From these measures, the number of cross-links created, factor G, was calculated, and it appeared to be proportional to temperature. Finally, we propose a new model tempting to explain the influence of temperature on the critical dose. It follows the formalism of transformation systems and has the advantage to match to the real mechanisms as described by chemists.

1. Introduction.

Polyethylene single crystals, like every organic substance, lose their crystallinity when they are hit by the electron beam during the observations in a microscope.

The critical dose of electrons for which the Bragg reflections disappear in the diffraction pattern is called $D_c$. On this dose depends the best expected resolution which varies as $(D_c)^{1/2}$ [1]. This dose can be increased by different ways. In a previous paper we reported how it is increased by the use of high accelerating voltages [2] and we discussed the accurate definition of the critical dose. Here we report a study on the effect of cooling the specimen down to 20 K at the same high voltages.

For lower voltages (100 to 1 000 kV), several authors noted an increase of the critical dose for temperatures down to 20 K. The increase rate depends on the specimen and varies between 1 and 5 for paraffin, polyethylene, aminoacids [3-8]. Experiments are in progress to determine if there is further improvement when the specimen lies in a cooled environment, i.e. when the lenses are cooled by liquid helium [9]. No measurement had yet been reported at high voltages.

Several authors [10-13] have noted that at room temperature the orthorhombic structure of polyethylene was changed into hexagonal structure during irradiation before being destroyed. We wanted to know what occurs at lower temperatures.

The reason why organic crystals are more resistant at lower temperatures is not clear and would involve many chemical investigations. Some papers show the important role of alkyl radicals and determine their rate of decay [14-19]. The cryo-protection has been attributed to the trapping of free radicals [6, 7] and this explanation agrees well with the chemical results. To explain the effect of temperature, only one model has been proposed, based on multiple hit theory [8].

In this study, we examine the effect of low temperature on the structure changes and on the critical doses of polyethylene single crystals at high voltages. Then we deduce information on the number of radicals produced according to temperature. Finally, we propose a new theoretical model of degradation, based on observations made by chemists, which
provides the intensity decrease of diffracted spots at different temperatures and the corresponding cross-linking rate.

2. Experimental observations.

2.1 Experimental details. — The specimens were prepared in suitable form for electron microscopy and the critical doses and critical times were measured on series of diffraction patterns as already described in part I [2]. The incident density on the specimen was 5 e/nm².s. The specimens were mounted upon a specimen holder cooled with liquid helium between 100 K and 20 K and observed at a voltage of 2 MV.

2.2 Influence of temperature on the critical dose. — The results of our measurements of the critical dose are reported in table I and in figure 1. As explained in part I [2], an uncertainty margin arises in these results from the fluctuations of the extremely low intensity of the incident beam. This is reported in figure 1.

It can be seen that the critical dose increases in the same way as at low voltages. The gain is effective below 100 K (factor × 2.2). At 20 K, the gain reaches × 4.2.

2.3 Changes of the crystalline unit cell. — At room temperature, the same transition from orthorhombic to hexagonal structure occurred like at lower voltage. The only difference is that the time scale is longer. So if this phenomenon is described with a normalized time or dose D/Dₜ, it seems to be independent of the voltage.

At lower temperatures (100 K and below) no transition is seen, at any voltage, 100 or 2 000 kV. The orthorhombic structure remains until the crystallinity is lost.

The question is now to explain how crystallinity is lost during irradiation in different ways according to the temperature and this is examined in the following section.

3. Evaluation of the cross-linking rate.

3.1 Cross-linking and loss of crystallinity. — When the electrons enter the specimen, primary events occur. There are collisions onto the atoms, during which a certain amount of energy is dissipated into the crystal. In part I [2], we described these primary events in detail and we calculated the stopping power dE/dx, that is the energy lost every length unit. We concluded that dE/dx is mainly dependent upon the electron energy, the geometrical structure of the crystal and its orientation with respect to the incident beam. The temperature T does not appear in its formulation because the primary collisions are not a priori affected by it.

Temperature acts on the secondary events following the primary collisions. Numerous secondary events may happen when the atom has been excited : chemical dissociation, fluorescence, phosphorescence, dissipation of heat [10, 20]. The two most important events with respect to our study is the formation of ions and radicals inside the crystal and in its superficial amorphous layer. They induce chemical reactions leading

<table>
<thead>
<tr>
<th>Temprature T, K</th>
<th>293</th>
<th>150</th>
<th>100</th>
<th>66</th>
<th>43</th>
<th>30</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical time t₀, s</td>
<td>406</td>
<td>682</td>
<td>897</td>
<td>1 136</td>
<td>1 375</td>
<td>1 554</td>
<td>1 710</td>
</tr>
<tr>
<td>Critical dose D₀, cb/m²</td>
<td>325</td>
<td>545</td>
<td>717</td>
<td>909</td>
<td>1 100</td>
<td>1 243</td>
<td>1 368</td>
</tr>
<tr>
<td>Critical dose D₀, e/nm²</td>
<td>2 031</td>
<td>3 408</td>
<td>4 484</td>
<td>5 679</td>
<td>6 875</td>
<td>7 772</td>
<td>8 548</td>
</tr>
<tr>
<td>Gain</td>
<td>1</td>
<td>1.68</td>
<td>2.21</td>
<td>2.80</td>
<td>3.39</td>
<td>3.83</td>
<td>4.21</td>
</tr>
<tr>
<td>Critical energy E₀, eV/nm³</td>
<td>523</td>
<td>879</td>
<td>1 156</td>
<td>1 464</td>
<td>1 773</td>
<td>2 004</td>
<td>2 204</td>
</tr>
<tr>
<td>G</td>
<td>0.6</td>
<td>0.357</td>
<td>0.271</td>
<td>0.214</td>
<td>0.177</td>
<td>0.157</td>
<td>0.142</td>
</tr>
</tbody>
</table>
either to chain scissions or to reticulations. These chemical processes are complex and a simple relation between the number of molecular events and the destruction of crystallinity does not seem to exist [21]. However several attempts have been made to describe the production and the decay of radicals on which depends the formation of cross-links and then, the loss of crystallinity [14-19].

At least three types of radicals have been detected during irradiation: alkyl radicals —CH₂CH₃—; allyl radicals —CH—CH═CH—; polyenyl radicals —CH—(CH═CH)ₙ—. A part of them recombine. It seems that cross-links are formed essentially from alkyl radicals, but some alkyl radicals can be changed into allyl ones. Radical pairs can be trapped inside the crystal, but some of them migrate towards the surface. Then they give rise to cross-links and lose hydrogen. Other cross-links are formed inside the crystal with a rate of 2 or 3 lower than in the amorphous part [19]. This can be summed up in the diagram of figure 2.

Cross-linking induces a structural transition, either because it introduces a fixed distortion or because the chains are far more mobile around a fixed position [19]. As irradiation proceeds, cross-linking rubs out the crystalline planes.

To explain the higher resistance at lower temperatures, it has been proposed that the radicals are trapped inside the crystal and cannot migrate to meet each other. Not so many cross-links are formed [5-8]. It can also be assumed that more excited atoms are restored in their neutral state.

These reactions are so complex — the diagram of figure 2 is just a simplification — that for practical reasons, they are usually reduced to the factor G, the number of cross-links produced when the primary collisions have transferred a 100 eV energy into the crystal. This factor varies with the structure of the crystal and its temperature.

It has been measured independently using other chemical techniques such as GPC by other authors at room temperature. They found a mean value $G = 1$ for bulk polyethylene, but it varies with crystallinity. Inside the crystalline part, G seems to be 0.6 at room temperature [19]. From our experimental results, we can calculate an approximate value for G at different temperatures.

3.2 THE CRITICAL ENERGY VARIES WITH THE TEMPERATURE. We call $R_c$ the number of cross-links per volume unit when the crystallinity has disappeared and $E_c$ the corresponding energy used to produce these cross-links. This energy is related to the critical dose by formula [2]:

$$E_c = D_c \frac{dE}{dx}. \quad (1)$$

As $dE/dx$ has been calculated at 2 MV in the preceding paper [2] and the values of $D_c$ have just been reported for different temperatures, we can calculate $E_c$. The results are reported in table 1. Of course, the variation follows the values of $D_c$ and it can be seen that this energy has values between 500 and 2 500 eV/nm³ at 2 MV.

3.3 EVALUATION OF $R_c$, THE CRITICAL NUMBER OF CROSS-LINKS. It is logical to assume that $R_c$, the number of cross-links necessary to lose the crystallinity is only related to the geometry of the crystal and does not depend upon the temperature or the voltage, because the diffraction pattern is only related to the position of atoms. It is a characteristic of the crystal.

$G$ is related to $R_c$ by the formula:

$$R_c = G \cdot \frac{E_c}{100} \quad (2)$$

where $E_c$ is expressed in eV.

We assume that $G = 0.6$ at 293 K (according to § 3.1) and $E_c = 523$ eV/nm³ (Table I).

Equation (2) leads to $R_c = 3.14$ cross-links/nm³ or about 0.3 cross-links per unit cell (see the unit cell in [2]). This value is slightly different from that, 0.575, found by Stenn and Bahr [20] for 100 keV electrons, but they did not take into account the difference for $G$ in bulk polyethylene and in single crystal.

3.4 EVALUATION OF $G$ AT VARIOUS TEMPERATURES. From formula (2) we deduce

$$G_T = G_{293} \frac{E_c(293)}{E_c(T)} = R_c \frac{100}{E_c(T)} \quad (3)$$
where \( G_{293} = 0.6, E_c(293) = 523 \text{ eV/nm}. \) The results are reported in Table I and in Figure 3.

It can be seen that the points are well aligned on a line of equation:

\[
G = aT + b.
\]

A statistical calculation by the least square method provides the best fit with \( a = 1.684 \times 10^{-3} \text{ T}^{-1} \) and \( b = 0.105 \) so that, between 20 and 293 K, we have:

\[
G = 1.684 \times 10^{-3} T + 0.105.
\]

### 3.5 Consequences on the Critical Dose

Resume now the different stages of our calculation and take them together in the formula giving \( D_c(1) \):

\[
D_c = E_c \frac{dx}{dE} = \frac{100 R_c}{G} \frac{dx}{dE}.
\]

At 2 MV, with \( R_c = 3.14, \) \( \frac{dx}{dE} = 0.258 \text{ eV/nm} \)

\[
D_c = \frac{100 R_c}{1.384 \times 10^{-6} T + 8.627 \times 10^{-3} (\text{e/nm}^2)}.
\]

In equation (5), \( \frac{dx}{dE} \) represents the dependence on the voltage and \( G = aT + b \) the dependence on the temperature.

### 4. A New Model of Damage Mechanism

To describe quantitatively the evolution of the radiation damage of organic substances with time we must know the number of undistorted cells as a function of time. This is true for radiation damage evaluated by the diffracted intensity where the undistorted cells are the crystalline unit cells, as well as for the loss mass or a chemical concentration of some element where the cells are the atoms themselves. Therefore a quantitative model must provide a law \( n = n(t) \).

Many empirical formulae have been proposed [22, 23] (see § 5.2) but they are no real models since the parameters involved have no physical reality and temperature is not taken into account. However we noted a few exceptions:

Some papers use the formula \( n = n_0 \exp(-\lambda t) \) [3, 24-27], which supposes a collision theory with a single hit: the probability of the collision, \( \lambda \), is proportional to the number of intact cells. This theory says nothing about the mechanisms leading to a loss of crystallinity and the influence of temperature \( T \) is not considered. Orth and Fischer [11], Grubb and Groves [5] then Reimer and Spruth [28] have represented the damage by a local disorder measured by a mean displacement distance \( u \). But we cannot predict any law \( u = u(t) \) or \( u = u(T) \).

The only model including the influence of temperature is the model by Reimer [8] developing ideas from Siegel [6] and Clark et al. [26]. This is a very interesting model because it gives a decreasing diffracted intensity with a very good agreement with experiment. Its fundamental physical process is still a collision but we are now dealing with a multiple target theory. That is \( m \) hits are necessary to be effective. So \( n/n_0 = 1 - \exp(-\lambda T)^m \). The important parameter \( m \) represents the influence of \( T \) since at low temperature \( m \) is greater. Reimer then could calculate the diffracted intensity and found the experimentally observed initial plateau and values of \( m \) reaching 4 to 8 between 20 and 50 K for various organic substances.

Unfortunately, this model does not represent the real chemical mechanisms leading to a loss of crystallinity as described in § 3.1. Therefore we tried to build a new model giving a law \( n = n(t) \) taking these mechanisms into account. Thus, we hoped to deduce information on the parameters governing these mechanisms. It is important to note that it is a general model that can be applied to any of these damaged systems and that our application to polyethylene single crystals is a first test for its validity.

To account for the decrease of \( G \) when \( T \) decreases, two chemical mechanisms have been put forward. The free radicals are trapped so that a self-healing process takes place [7], or the radicals migrate more slowly [17]. We think that these mechanisms, schematised in Figure 2, can be best treated by the theory of transformation systems [29] which provides a coherent tool, far closer to the real mechanisms than the previous models. Within this frame, we attempted to evaluate numerical values for the rate of transformation of radicals to cross-link according to temperature.

Note that Figure 2 is already a simplification of the real mechanisms and that however, a great number of parameters remains, so many that significant results will be obtained only by a more severe simplification. Some indications were given to us by the authors who measured the decay of alkyl radicals remaining after
irradiation [14-19]. They fit their decay curve by the sum of two decreasing exponentials, a slow decay and a rapid one [16, 17, 19]. The fast decay seems to come from radicals that have not to migrate to recombine. The slow decay is attributed either to reactions of isolated radicals or to radicals which have to migrate. Nothing is known about the self healing rate of excited atoms to neutral atoms.

4.1 GENERAL MODEL. — The formalism of transformation systems describes the evolution of systems, the elements of which can be separated into homogeneous classes. We represent our real object by a theoretical system with 5 classes $C_1, C_2, C_2', C_2$ and $C_3$ and this is a simplification with respect to figure 2 (Fig. 4) $N_1$ is the number of neutral atoms, $N_2$ the number of alkyl radicals in crystalline part, $N_2'$ and $N_2''$ the number of two other sorts of radicals, and $N_3$ the number of atoms which have moved by cross-linking. The arrows show the possible transformations.

Since the parameters are numerous, we think that, whatever the model, it can be easily fitted to experimental results. That is why so many different empirical formulae have been proposed. That is why a good fit to experimental data is not a sufficiently reliable criterium of validity for this model.

Here we intend only to evidence how the existence of several classes and several rates of transformation between them can influence the evolution of the general system and how the different formulae previously proposed can appear as particular cases of this general model.

From this point of view it is instructive to limit this model to three classes only according to the diagram of figure 5, where we keep $C_2$, but neglect $C_2'$ and $C_2''$ which are not directly related to the formation of cross-links.

The transformation of neutral atoms $N_1$ into radicals $N_2$ is represented by $s$, which is closely related to $\sigma_10$, the cross section of neutral atoms to be excited by inelastic events. These radicals can be restored to the original neutral atoms with a rate $x$. How fast these radicals are transformed into cross-links by some migration along the chains inside the crystal is given by $y$. $s$, $x$ and $y$ are expressed by a number per time unit.

Then, we have:

$$\begin{align*}
\dot{N}_1 &= -sN_1 + xN_2 \\
\dot{N}_2 &= sN_1 - (x + y)N_2 \\
\dot{N}_3 &= yN_2 
\end{align*}$$

At time $t = 0$, $N_1 = N_0$, initial number of neutral atoms and $N_2 = N_3 = 0$.

We find:

$$\begin{align*}
q_1 &= \frac{x + y - s + p}{2p} \ln e^{-\lambda_1 t} + \frac{x - y + s + p}{2p} \ln e^{-\lambda_2 t} = \frac{\lambda_2 - s}{p} e^{-\lambda_1 t} + \frac{-\lambda_1 + s}{p} e^{-\lambda_2 t} \\
q_2 &= \frac{s}{p} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \\
q_3 &= \frac{ys}{p} \left(\frac{1}{\lambda_2} e^{-\lambda_2 t} - \frac{1}{\lambda_1} e^{-\lambda_1 t}\right) + 1 = \frac{ys}{p} \left[\frac{1}{\lambda_1} (1 - e^{-\lambda_1 t}) - \frac{1}{\lambda_2} (1 - e^{-\lambda_2 t})\right]
\end{align*}$$

where we have put:

$$\begin{align*}
q_1 &= N_1/N_0; \quad q_2 = N_2/N_0; \quad q_3 = N_3/N_0 \\
p &= [s^2 + 2s(x - y) + (x + y)^2]^{1/2} \\
\lambda_1 &= \frac{(x + y + s) - p}{2}; \quad \lambda_2 = \frac{(x + y + s) + p}{2} = \lambda_1 + p \\
\lambda_1 \quad \text{and} \quad \lambda_2 \quad \text{are positive and} \quad \lambda_1 < \lambda_2.
\end{align*}$$

We can also change the variables and take $st = u$, $\alpha = x/s$, $\beta = y/s$. The reason is that $s$ is not a priori temperature dependent and is a time scaling variable. Then,

$$\begin{align*}
r &= p/s = [1 + 2(\alpha - \beta) + (\alpha + \beta)^2]^{1/2} \\
\lambda_1 &= \frac{s}{2} (\alpha + \beta + 1 - r) = l_1 s \\
\lambda_2 &= \frac{s}{2} (\alpha + \beta + 1 + r) = l_2 s
\end{align*}$$

Fig. 4. — A 5-class model of radiation damage. The arrows point a possible transformation. $I_i$ is the incident intensity.

Fig. 5. — A 3-class model of radiation damage. Letters denote the transformation rates.
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\[
\begin{align*}
q_1 &= \frac{l_2 - 1}{r} e^{-l_1w} + \frac{l_1 + 1}{r} e^{-l_2w} \\
q_2 &= \frac{e^{-l_1w} - e^{-l_2w}}{r} \\
q_3 &= \frac{B}{r} \left[ \frac{1}{l_1} (1 - e^{-l_1w}) - \frac{1}{l_2} (1 - e^{-l_2w}) \right]
\end{align*}
\]

(9)

\(l_1\), \(l_2\), and \(r\) are independent from \(s\) so that only two parameters remain.

We have obtained the evolution with time of a population \(q_1\), \(q_2\) or \(q_3\) and the temperature acts through two parameters \(\lambda_1\) and \(\lambda_2\). The consequences will be discussed in § 5, but now, we want to restrict ourself to the damage evaluated by the diffracted intensity.

**4.2 Calculation of the diffracted intensity.**

In the case of a crystal, the relation between the diffracted intensity and the number of diffracting atoms is rather complex and cannot generally be expressed in an analytic form. If the diffraction pattern is composed of many beams, the intensity can only be calculated numerically [2]. In these simulations, it is easy to take absorption into account [2]. But, in order to understand the role of temperature, we consider a particular case when we have only one diffracted beam and we are in Bragg conditions. These conditions lead us to a simple analytic form and to valuable information. Absorption can be neglected because our specimen is very thin [2]. The restriction to Bragg conditions is not so easy to justify. Jouffrey found a different intensity decrease according to orientation by numerical simulation [27]. However, besides the fact that we can obtain an analytical form only in the Bragg position — as will be reported later — it can be noted that the areas contributing to the diffracted spot intensity are essentially in the Bragg position.

In the two-beam conditions, the diffracted intensity is of the form [30]:

\[
I = I_1 \frac{\sin^2 \pi \pi z \sigma}{\pi^2} \xi^2
\]

(10)

where \(z\) is the thickness, and \(\sigma\) and \(\xi\) are functions of the orientation and structures of the crystal. For thin specimens,

\[
I \approx I_1 \frac{\pi^2}{\xi^2} z^2.
\]

For polyethylene \(\xi\) is estimated to 300 nm at 2 MV (see Table II) compared to \(z\) of the order of 10 nm, so that this approximation is valid.

The damaged cells are amorphous and can therefore be considered as an inclusion of a precipitate of thickness \(z_1\) in the crystalline matrix. Guyot [31] could calculate the contrast of such inclusions and showed that in the particular case of Bragg conditions, the inclusion induced no change in phase so that the intensity was the same as that of a crystal with thickness \(z - z_1\):

\[
I = I_1 \frac{\pi^2}{\xi^2} (z - z_1)^2.
\]

(11)

As a first approximation we consider that \(z_1\), the thickness of the amorphous inclusion, is proportional to the number of crosslinks and \(z - z_1\) is proportional to the undisplaced atoms, that is \(q = q_1 + q_2\). Then

\[
I = I_0 q^2 = I_0(q_1 + q_2)^2.
\]

(12)

In amorphous solids, the diffused intensity is proportional to the number of atoms because partial intensities are added, but in crystals, where there are phase relations between the diffracted waves, amplitudes are added so that the intensity varies with the square of the atom number.

We find:

\[
q = q_1 + q_2 = (l_2/r) e^{-l_1w} - (l_1/r) e^{-l_2w}
\]

(13)

thus

\[
I = I_0[(l_2/r) e^{-l_1w} - (l_1/r) e^{-l_2w}]^2 =
= I_0[(l_2/r)^2 e^{-2l_1w} + (l_1/r)^2 e^{-2l_2w} - (2 l_1 l_2/r^2) e^{l_1 + l_2w}].
\]

(14)

Typical curves of \(I/I_0\) are reported in figures 7 and 8 for different values of \(\alpha\) and \(\beta\). In figure 7, we can see that the form of the curves suits well with experimental results (Fig. 9) with its initial plateau. When \(\beta\) increases, the form is similar but the intensity decreases faster, and the plateau becomes shorter. When \(\alpha\) increases (Fig. 8) on the contrary, the crystallinity remains a longer time but this is sensible only for values of \(\alpha\) greater than 0.5.
This formalism has been tested on two typical experimental curves of decreasing intensity (Fig. 9), that have been depicted from a series of diffraction micrographs as described in part I [2]. They can be divided into two parts. For \( t > t_1 \) (where \( t_1 \) is about 0.6 \( t_c \)), we have an exponential decay. If we draw it in logarithmic coordinates, the slope is given by 2 \( \lambda_1 \). If we subtract this term from the whole curve, the remaining value can be fitted by two other decreasing exponentials, one with a slope 2 \( \lambda_2 \) and the other one with a slope not very far from \((\lambda_1 + \lambda_2)\). The knowledge of \( \lambda_1 \) and \( \lambda_2 \) gives numerical values for \( x + y + s \) and \( sy \).

Unfortunately, the accuracy on \( \lambda_2 \) is bad because the first part of the curve \((t < t_1)\) is fluctuating from a crystal to another so that comparisons are not strictly valid. Therefore, we were not able to make clear how the parameters \( x \) and \( y \) are affected by temperature. We could however demonstrate that these curves can be fitted by our model with values of the parameters of the order of:

\[
\begin{align*}
\lambda_1 &\approx 4 \times 10^{-4} \text{ s}^{-1} \\
y &\approx 10^{-2} \text{ s}^{-1} \\
x &\text{very low}
\end{align*}
\]

\( s \) can be compared with the calculated value \( s = \sigma l_0 = 2 \times 10^{-4} \text{ s}^{-1} \) at 2 MeV.

### 4.3 The Critical Time

The critical number of crosslinks, \( R_c = 0.3 \) per unit cell (see § 3.3) is reached at a time \( t_c \) measured in § 2.2 and reported in table I. As this time,

\[
q_3 = q_c = \frac{\beta}{r} \left[ -\frac{1}{l_1} e^{-l_1 u_c} + \frac{1}{l_2} e^{-l_2 u_c} \right] + 1
\]

so that

\[
-\frac{1}{l_2} e^{-l_2 u_c} + \frac{1}{l_1} e^{-l_1 u_c} = (1 - \sigma l_0) \frac{r}{\beta}
\]

or

\[
sy \left[ \frac{1}{l_1} e^{-l_1 u_c} - \frac{1}{l_2} e^{-l_2 u_c} \right] = (1 - \sigma q_c) p \quad (15)
\]

with \( q_c = 2 R_c/N_0 = 0.15 \), if we suppose that 2 atoms are displaced in a crosslink. Equation (15) gives \( sy \) if \( \lambda_1 \) and \( \lambda_2 \) are given by (14).

It can be verified that the numerical values found in § 4.2 and table I are coherent with equation (15).

### 5. Discussion

The validity of our model can be tested on several criteria, the first of them being the fit with our experiences. But, owing to the great generality of this model, other criteria will be examined [29].

#### 5.1 Adjustment to Experimental Data

We are aware that our experiments are much too crude to prove the validity or refute our model. The reason
for this is that it is impossible to control the incident intensity at so small a value. It is necessary now to record the same decreasing diffracted intensity on a microscope whose beam intensity is well monitored and integrated over time.

Nevertheless, it can be first observed that the general form of the experimental curve has been obtained and that the values of the parameters are of the right order of magnitude. Up to now only the model of Reimer [8] has provided the initial plateau, but we already mentioned that we have tried to have a model built on the real chemical mechanisms. Furthermore, our plateau would be more pronounced if not only three classes of elements had been retained. That is, it is possible to sophisticate the model.

5.2 COHERENCE. — Now we examine the validity of the general model given at the end of § 4.1 (Eqs. (8) and (9)), that is the formulae giving the number of atoms of each class. These formulae can be applied in a great variety of systems. In fact, we have simplified our initial system of figure 2 to those of figures 4 and 5 so that any system analogous to figure 5 can be described by our model. Not only the decreasing diffracted intensity is susceptible of such a description: the chemical composition in organic and biological systems, crystalline or amorphous ones, varies according to the same rules (Eq. (9)). Two precautions must be taken. First the passage from the number of elements \( q \) to the measured quantity: The diffracted intensity in a crystal is proportional to \( q^2 \) (see § 4.2) but the K X-ray peak intensity of an element is proportional to \( q \), the number of atoms of this element. Second, formula (9) with its 2 exponentials reflects the number (3) of classes in figure 5. In the model of figure 4 with 5 classes, we should have obtained a \( q^3 \) value with 4 exponential terms. The number of exponentials is an indication of how many classes are active. Indeed, most of the empirical laws proposed by different authors appear as particular cases of our model. Let us take some examples, most of them reviewed in an excellent paper by Vesely [22].

To account for the chlorine loss in amorphous PVC, Vesely has proposed:

\[
I/I_0 = e^{-k_1D} + B(e^{-k_1D} - e^{-k_2D}).
\]  
(16)

This formula with three decreasing exponentials shows that at least four classes of elements in figure 4 are active.

On the other hand, we understand that if the formula of Egerton [23]:

\[
I/I_0 = e^{-D/D_1} + e^{-D/D_2}
\]  
(17)

is not in accordance with experimental results, as noted by Vesely [22], it is because at least one coefficient is missing.

Formula (16) is sometimes simplified [22] into:

\[
I/I_0 = (1 - A) e^{-k_1D} + A e^{-k_2D} 
\]  
(18)

or

\[
I/I_0 = (1 - A) e^{-kD} + A .
\]  
(19)

Equation (18) is found in our formalism when \( \alpha = 0 \) (no self healing).

Then \( l_1 = \beta, l_2 = 1 \)

\[
q = \frac{1}{1 - \beta} e^{-\beta u} - \frac{\beta}{1 - \beta} e^{-u} = \\
= \frac{1}{1 + \beta} e^{-\sigma D l_1} - \frac{\beta}{1 - \beta} e^{-\sigma D} .
\]  
(20)

Then, for an amorphous material, we can identify:

\[
A = \frac{1}{1 - \beta}, k_1 = y/l_1, k_2 = \sigma .
\]

Formula (19) is found when all radicals immediately crosslink, so that \( q_1 \) is the number of diffracting atoms, \( q_2/2 \) the number of crosslinks, \( y = 0 \) (Fig. 5). We find:

\[
q_1 = \frac{\alpha}{\alpha + 1} + \frac{1}{\alpha + 1} e^{-\alpha l + \alpha w}.
\]  
(21)

We can identify:

\[
A = \frac{\alpha}{\alpha + 1}, k = \frac{x + s}{I_1}.
\]

At last, the decreasing intensity is often fitted by a single exponential law [7, 24, 26]:

\[
I/I_0 = \exp(-D/D_\varepsilon) .
\]  
(22)

This formula implicitly supposes a mechanism with no self-healing and immediate crosslinking of radicals \( \alpha = 0, \beta = 0 \) in formula (21)), so that

\[
q_1 = e^{-u} = e^{-\sigma D}.
\]  
(23)

5.3 EXTERNAL RATIONALITY. — All formulae given by other authors are phenomenological, that is, parameters like \( k_1, k_2, D_e \), have received no physical interpretation, because they are not related to a precise molecular mechanism. However, the model of Reimer is supported by a molecular mechanism: \( m \) hits are necessary to destroy the target cell or produce an excited state. From this mechanism we have deduced another formula if we adopt the diagram of figure 6. A proportion \( k \) of atoms return to their initial state so that \( k = (m - 1)/m \)

\[
\left\{ \begin{array}{l}
\dot{N}_1 = - s(1 - k) N_1 = - \frac{s}{m} N_1 \\
\dot{N}_2 = - \dot{N}_1 \\
q_1 = e^{-u/m} \\
q_2 = 1 - e^{-u/m} .
\end{array} \right.
\]  
(24)

When the temperature decreases, \( m \) increases.
So our model has the advantage to propose an explanation of the influence of temperature based on the real mechanism described by chemists (Fig. 2).

5.4 Predictions. — Contrary to all formulae proposed by different authors, our model depends on the variable $t$ and not $D$. We showed that they are equivalent only in the simplified models (20), (21), (23), (24), but not in the general case. So, the intensity decrease depends \textit{a priori} on the incident intensity $I_i$, a result not predicted by any other formulae. This result has been theoretically demonstrated for general transformation systems [29]. No experimental proof of this influence has been given yet for polymers [10, 32] but it can be noted that the range of variable intensity lies only over 1 order of magnitude and that, if our specimen is comparable to living cells [29], an effect would be detected only when the intensity is changed by a factor of 100 or 1 000. Thus, this prediction is very important for the use of STEM where the beam is very concentrated and for the use of pulsed beams. It would be interesting to compare the diffracted intensity of crystals under these conditions.

6. Conclusion.

We have shown that there is an effective cryoprotection of polyethylene at high as well as at low voltages and the life time is 4 times longer at 20 K than at 300 K.

Below 100 K no hexagonal intermediate crystalline phase is observed. From our calculations of the stopping power, and using a measure of the factor $G$ at 300 K, we have shown that $G$ is a linear function of $T$ between 20 K and 300 K and that 0.3 crosslinks per unit cell are requested to destroy crystallinity.

We propose a general model that can account for the intensity decrease of the diffracted spot and the increase of life time at lower temperatures. With respect to the model of Reimer, it has the advantage to match the real mechanisms. It predicts a dependence of the critical dose on the incident intensity. Finally, it could be possible to apply this model to various organic, biological, crystalline, amorphous systems, (measurements of diffracted intensity, of element concentration or mass loss). The only requirement is that these systems are composed of a few classes exchanging their elements. This is why various empirical laws have appeared as particular cases of our model.

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References

[29] Delattre, P. and Delforge, J., La théorie des systèmes de transformation, application à la radiobiologie.

