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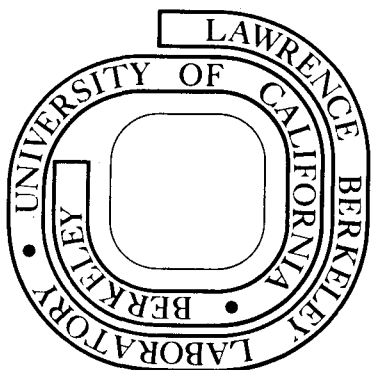
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ELECTRON DAMAGE IN ORGANIC CRYSTALS

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ABSTRACT

The effects of radiation damage in three crystalline organic materials have been investigated by electron microscopy.

The degradation of these materials has been found to be consistent with a gradual collapse of their crystal structures brought about by ionization damage to the comprising molecules.

It is inferred that the crystallinity of these materials is destroyed by ionizing radiation because the damaged molecules cannot be incorporated into the framework of their original structures.

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INTRODUCTION

Radiation damage is a fundamental limitation to the application of electron microscopy in the study of organic materials⁽¹⁾ and more information is needed concerning the details of the mechanism of specimen degradation.

In this investigation three organic materials l-valine⁽²⁾, cytosine⁽³⁾ and copper phthalocyanine⁽⁴⁾ were examined under in-situ irradiation in the electron microscope and their structural behaviour was compared with the available radiochemical data.

In l-valine and cytosine radiation damage in the dry state is known to be dominated by fragmentation about the functional groups⁽⁵⁾⁽⁶⁾ whilst in copper phthalocyanine fission of the outer conjugated rings and hydrogen bond rupture are the most likely events⁽⁷⁾.

EXPERIMENTAL DETAILS

Large single crystals of L-valine and cytosine, suitable for electron microscopy, were prepared on formvar coated copper grids by the dropwise evaporation of dilute solutions. L-valine was prepared from an aqueous solution whilst, to prevent the formation of cytosine monohydrate, cytosine was prepared from an ethanolic solution. Single crystals of copper phthalocyanine were deposited onto similar grids from an ethanolic suspension of finely ground powder.

The specimens to be observed solely in diffraction were vacuum deposited with gold to calibrate their lattice spacings and all the specimens were examined at 100 keV in a Siemens 102 electron microscope under a constant beam current to the specimen. In this way the behaviour of the specimen could be compared with the radiation dose that it had sustained.

The critical exposures of the materials were measured using a Faraday cup⁽⁸⁾ and, during experimental observations, the exposure sustained by any crystal was determined as a fraction of this dose at the particular current density.

The high resolution images were recorded at a magnification of 100,000 x from a symmetrically oriented $\langle 100 \rangle$ diffraction pattern with the transmitted beam aligned to the optic axis of the microscope. The contribution of six (00L) beams to these images was established by optically transforming the original electron micrograph.

The image and diffraction patterns were recorded on Kodak 4489 sheet film and developed in 50% diluted D-19.

RESULTS

The critical exposures of l-valine, cytosine and copper phthalocyanine were determined to be 3×10^{-3} , 4×10^{-2} and 3 Coulombs cm^{-2} respectively to 100 keV electrons.

The degradation of these materials, prior to their total loss of crystalline diffraction is characterized by a change in spacing of some of the diffraction spectra and the magnitude of these variations, in terms of real space parameters, is shown in table I. These variations are independent of the specimen orientation to the incident electron beam and can be consistently interpreted for each material as an unique deformation of the crystal lattice.

In copper phthalocyanine the lattice deformation involves an expansion of the unit cell along [100] and a contraction along [001]. In cytosine there are contractions along [100] and [010] and in l-valine there is a dominant contraction of the unit cell along [001].

The [001] direction in l-valine and the [010] and [100] directions in cytosine are those along which the unit cells would collapse if the functional groups of the molecules were to be removed (figure 1a, 1b) whilst in copper phthalocyanine [100] is significant because the molecules stacked in this direction sustain the shortest intermolecular distance.

The shortest intermolecular distance is indicated in figure 1c and is that between a carbon atom in an outer conjugated ring and a nitrogen atom in the core of its neighbour. Increasing this intermolecular separation, which could arise from fission to the conjugated ring, would predominantly increase the interplanar spacings of $(20\bar{1})$ and (100) which is the deformation observed.

In all these materials therefore the structural modifications which are observed can be attributed to the response of a unit cell in accomodating the most likely fragmentation events.

The magnitude of the electron dose necessary to initiate a detectable structural modification to these materials is about a tenth of the critical exposure and in figure 2 the changes in spacing of twelve separate (20 $\bar{1}$) reflections of copper phthalocyanine are shown as a function of electron dose.

In copper phthalocyanine it is also possible to observe the radiation damage directly by high resolution lattice imaging and in figure 3 lattice images from the (001) planes, recorded almost immediately after the specimen was exposed to the electron beam, illustrate the characteristic specimen deterioration. The resolution in these images is better than 4 \AA and an electron dose to the specimen of about 1C.cm^{-2} was necessary to record them. The photographs were all processed from the same micrograph and are at different magnifications to illustrate the size distribution of the radiation damaged regions.

DISCUSSION

The fragmentation processes which occur in a material can be quantitatively determined by radiolysis in terms of both the total number of fragmentation events (G_M) and the number of individual fragmentation products A, B, C... ($G_A G_B G_C$) which result from the absorption of 100 ev of energy from the primary beam.

The energy loss rate of a 100 kev electron traversing a thin specimen can be calculated readily from stopping power theory⁽⁹⁾ and hence the concentration of fragmentation products at any dose can be predicted from a survival curve⁽¹⁰⁾ of the form

$$S = S_0 e^{-D/D_{37}}$$

where S_0 is the number of molecules in the specimen, S is the number which survive fragmentation after an electron dose D, and D_{37} is the electron dose

equivalent needed to produce an average of one such fragmentation event per molecule. In reality 37% of the molecules are intact at this dose because some of the 63% have suffered more than one interaction.

When the electron doses are in units of electrons cm^{-2}

$$D_{37} = \frac{100Nm}{G} \left[\frac{dE}{dx} \right]^{-1}$$

where Nm is the volume density of molecules and $\frac{dE}{dx}$ is the energy loss rate of a 100 keV electron in ev cm^{-1} .

The radiolytic yield of L-valine has been determined by Gejvall and Lofroth⁽⁵⁾ and a total degradation (G-M) of 8 was established. The total degradation yield is almost entirely derived from fragmentation across the functional groups whilst small amounts of methane, ethane and propane were also reported which is characteristic of the fragmentation of the carbon chain. These products were assessed to be a minor component of the hydrocarbon yield, which was assigned a G value of 0.2.

It is apparent from the survival curves corresponding to these G values which are plotted in Fig. 4 that fragmentation of the carbon chain cannot account for the value of the critical exposure in L-valine since substantially fewer than 3% of the molecules have been affected in this way by this dose. The onset of structural deformation at an electron dose of $3 \times 10^{-4} \text{ Ccm}^{-2}$ and its progression to the critical exposure at $3 \times 10^{-3} \text{ Ccm}^{-2}$ are however readily interpreted in terms of fragmentation about the functional groups, since at these doses 20% and 90% of the molecules in the specimen have sustained such an event.

The radiolytic yield of cytosine has not been determined in the dry state however those aromatic compounds which have been analysed invariably exhibit a total degradation yield between 0.2 and 1.0⁽⁶⁾. The electron dose which corresponds to the critical exposure of cytosine would fragment 90% of the molecules in a material where the total degradation yield is 0.7.

Copper phthalocyanine is sufficiently stable that the changes in interplanar spacing can be determined as a function of electron dose and so compared directly to the single hit target model.

The change in spacing of twelve separate (20 $\bar{1}$) planes is shown in figure 2 and when these variations are averaged and set proportional to the number of damaged molecules their behaviour closely follows a survival curve corresponding to a G value of 0.004 and a destruction of 99% of the molecules at the critical exposure (figure 4).

Whilst the loss of crystallinity in l-valine and cytosine can be satisfactorily explained by the depleted concentration of perfect molecules, copper phthalocyanine may not be so straight forward to interpret since 0.004 is an extremely small value for the total degradation yield of an aromatic compound.

In addition to its ability to induce ionization damage, which results from electron-electron collisions, a 100 keV electron is also capable of destroying the structure of an organic compound by displacing the atoms directly in electron-atom collisions. This knock-on damage is extremely rare in comparison to the number of electron-electron collisions which occur. However, in a material such as copper phthalocyanine, which is extremely resistant to ionization damage, this type of radiation damage must be considered.

The role of displacement damage by the electrons can also be considered in terms of a survival curve since the cross section for a particular event is the inverse of the electron dose equivalent needed to produce it.

The appropriate survival curve is therefore described by

$$S = S_0 e^{-D\sigma/n}$$

where σ is the total displacement cross section offered by a molecule in cm^2 and n is the average number of displacements which will destroy it.

The direct displacement survival curve for copper phthalocyanine shown in figure 4 corresponds to a total displacement cross section of $2.4 \times 10^{-21} \text{ cm}^2$ where one displacement event is sufficient to destroy the molecule ($n = 1$).

The total cross section was obtained by summing the calculated cross sections of the constituent atoms to 100 kev electrons⁽¹¹⁾ assuming the threshold energy for the displacement of a single atom to be the product of its valency with an average bond energy of 4 ev.

The degree of displacement damage, based on these cross sections, is too low to contribute significantly to the radiation damage of this material involving less than 5% of the molecules at a dose equal to the critical exposure. The radiation damage of copper phthalocyanine must therefore also be induced by ionization damage.

The nature of the ionization processes in an organic material has been considered by Magee⁽¹²⁾, who describes it in terms of spurs, blobs and short tracks being induced by the primary electron from energy loss events of 0-100 ev, 100-500 ev and 500-5000 ev. These processes describe the behavior of the secondary electrons whose range confines the size and distribution of these events, not exceeding 15Å for a spur, 120Å for a blob or 7000Å for a short track. In the complete absorption of a 1 Mev electron Magee estimates the ratio of spurs : blobs : short tracks to be 500 : 5 : 1.

The high resolution lattice images from the (001) planes of copper phthalocyanine (figure 3) indicate that the destruction of crystallinity, which is characterised by the absence of the lattice period, is induced by events whose influence extends over a range of dimensions from as large as 1000Å to as small as 50Å. In addition the contrast from the lattice images as a whole is suggestive of radiation damage on a much finer scale being widespread over the whole specimen.

The high resolution lattice images of copper phthalocyanine (figure 3) can be interpreted according to the description of Magee if the fine scale modification is attributed to spurs and those of larger dimension to blobs or short tracks.

It is noteworthy that as the regions of damage become larger their projected shape becomes elongated which is suggestive of the progression from blob to short track as the energy of the secondary electron increases.

SUMMARY

The radiation damage of organic materials in the electron microscope has been shown to be structurally consistent with the sequential replacement of the comprising molecules by their fragmentation products at a rate consistent with their radiolytic yields and by a mechanism appropriate to ionization damage.

In l-valine and cytosine it has been shown that even a singly fragmented molecule cannot be accommodated in the crystal lattice whilst in copper phthalocyanine this can only be confirmed by a determination of the radiolytic yield.

The degree of direct displacement damage, in even the most resistant of these materials, has been shown to be too small to be responsible for the radiation damage which is observed. The large differences between the critical exposures of the materials examined reflects only their resistance to ionization damage.

ACKNOWLEDGEMENTS

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TABLE 1

The interplanar spacings and lattice parameters of copper phthalocyanine, cytosine and l-valine measured by diffraction in the electron microscope.

The values marked with an asterisk are characteristic of radiation damaged material.

TABLE I ELECTRON DIFFRACTION MEASUREMENTS OF THE CRYSTAL STRUCTURES

	COPPER PHTHALOCYANINE			CYTOSINE			L-VALINE		
	X-ray ⁽³⁾	Electron Diffraction		X-ray ⁽²⁾	Electron Diffraction		X-ray ⁽¹⁾	Electron Diffraction	
	$\pm 0.01 \text{ \AA}$	MAXIMUM $\pm 0.1 \text{ \AA}$	MINIMUM $\pm 0.1 \text{ \AA}$	$\pm 0.01 \text{ \AA}$	MAXIMUM $\pm 0.1 \text{ \AA}$	MINIMUM $\pm 0.1 \text{ \AA}$	$\pm 0.01 \text{ \AA}$	MAXIMUM $\pm 0.1 \text{ \AA}$	MINIMUM $\pm 0.1 \text{ \AA}$
d_{001}	12.57	12.8	12.4*						
$d_{20\bar{1}}$	9.63	10.3*	9.6						
d_{100}	16.88	21.0*	16.8				9.71	9.7	8.9*
d_{010}	4.79	4.9*	4.8	9.49	9.5	9.3*	5.27	5.3	4.9*
d_{110}	4.61	4.8*	4.6	7.67	7.7	7.5*	4.63	4.6	4.3*
$d_{11\bar{1}}$	4.54	4.6*	4.5	3.42	3.4	3.4*	4.33	4.4	3.9*
$d_{21\bar{1}}$	4.29	4.3*	4.3						
d_{021}	2.35	2.4*	2.3						
$d_{10\bar{1}}$				3.66	3.7	3.6*			
d_{210}							3.57	3.6	3.2*
d_{011}							4.82	4.8	4.3*
a	19.6	22.9*		13.04	12.8*		9.71	8.9*	
b	4.79	4.9*		9.49	9.3*		5.27	4.9*	
c	14.6	13.6*		3.81	3.8*		12.06	9.2*	
β	120.6*	13.6*					90.8°	90°*	
Unit Cell	1179.8 \AA^3	1397 \AA^3		472.3 \AA^3	452 \AA^3		617.2 \AA^3	401 \AA^3	
Volume									

FIGURE CAPTIONSFigure 1

Projections of the unit cells of a) cytosine b) l-valine and c) copper phthalocyanine, illustrating the locations of the molecules. The shortest intermolecular distance in copper phthalocyanine is arrowed and is between molecules whose alternate inclination is disguised by the projection.

Figure 2

The change in the $(20\bar{1})$ interplanar spacing of copper phthalocyanine as a function of electron dose. The measurements were made from twelve separate diffraction patterns from specimens which were coated with a thin layer of evaporated gold for calibration.

Figure 3

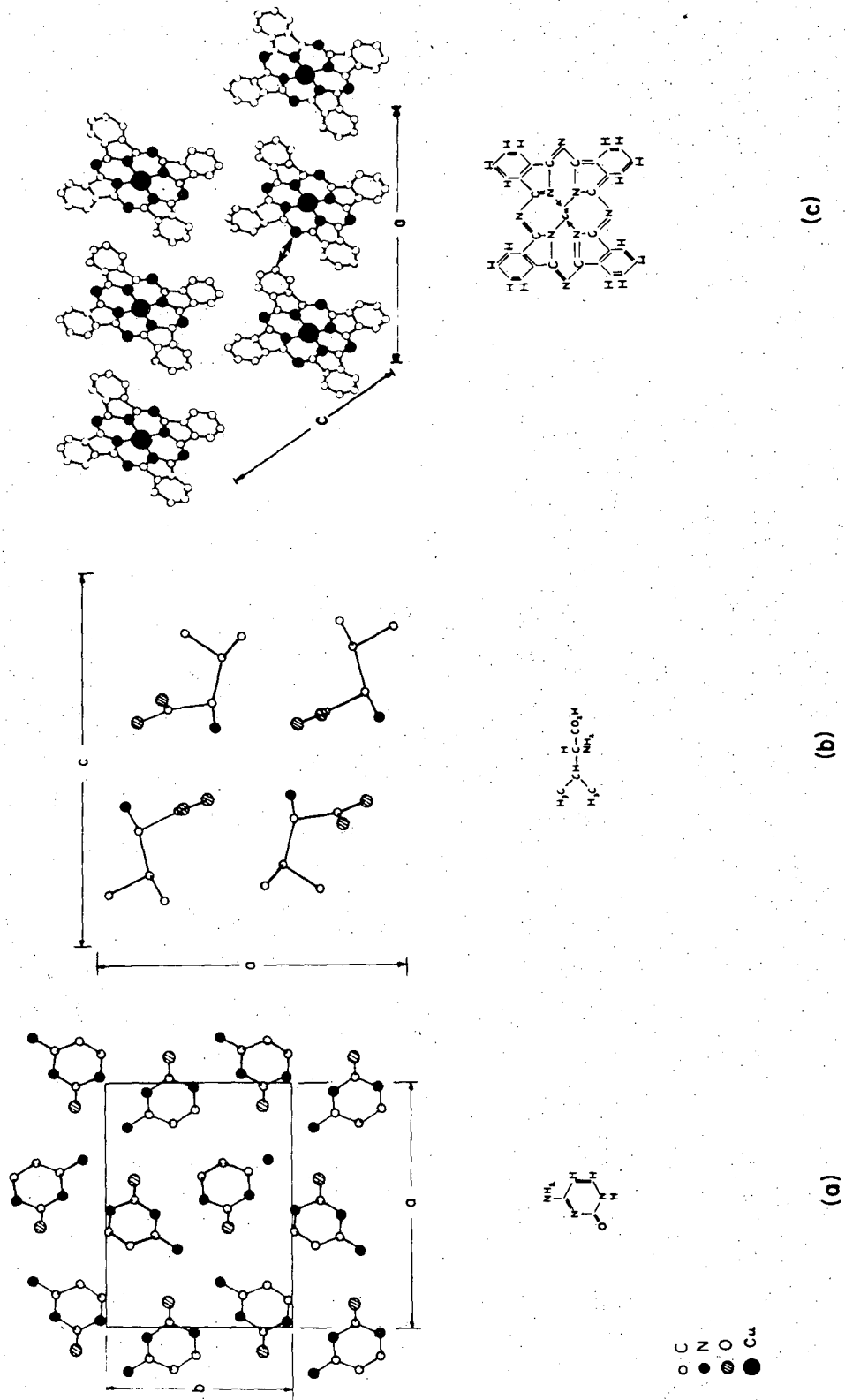
Lattice images from the (001) planes of copper phthalocyanine showing the extent and distribution of the structural collapse.

The photographs were all processed from the same micrograph and the appropriate dimensions corresponding to the extent of blobs and spurs are indicated.

Figure 4

Survival curves relating the proportion of molecules in the specimen hosting radiation damage to the electron dose received. The particular curves relate to the various types of radiation damage considered in the text. In the case of direct displacement a damaged molecule is one which has suffered knock-on of at least one of its constituent atoms regardless of type.

The average spacing of the (201) planes of copper phthalocyanine as a function of electron dose is also shown in the lower figure.



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FIG. 1

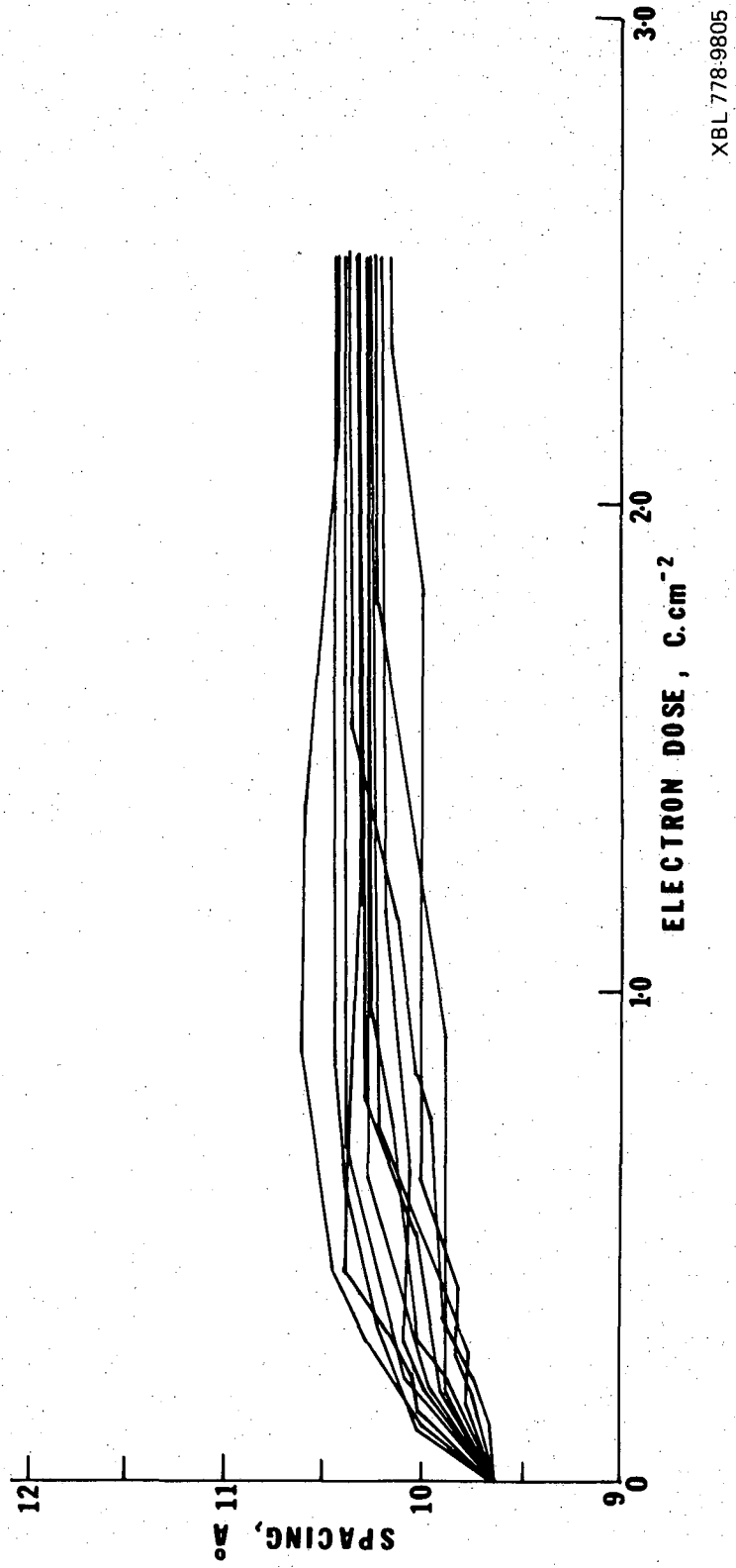
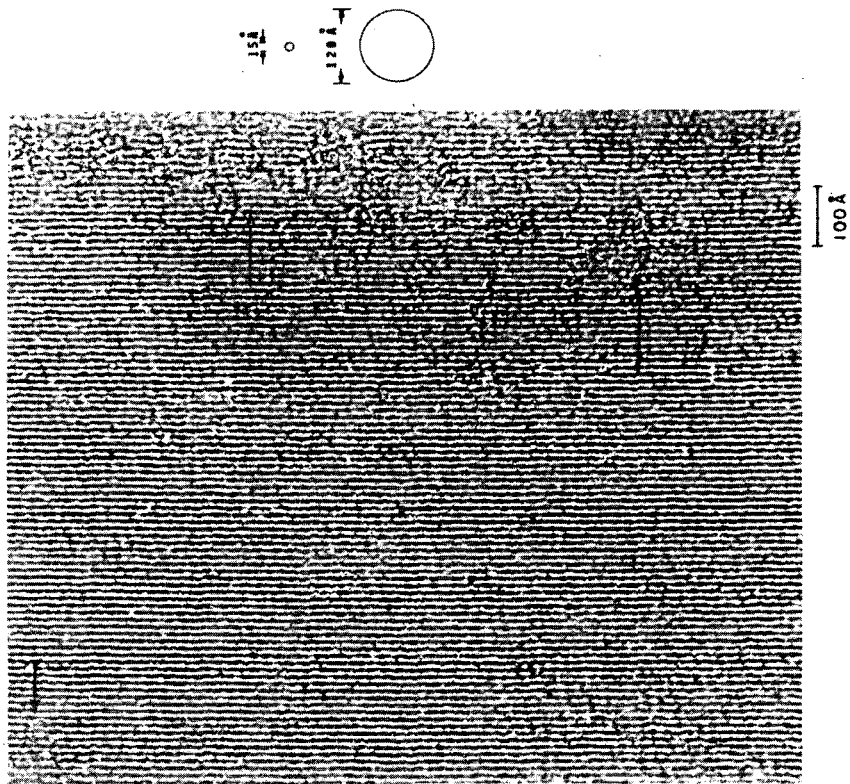


FIG. 2



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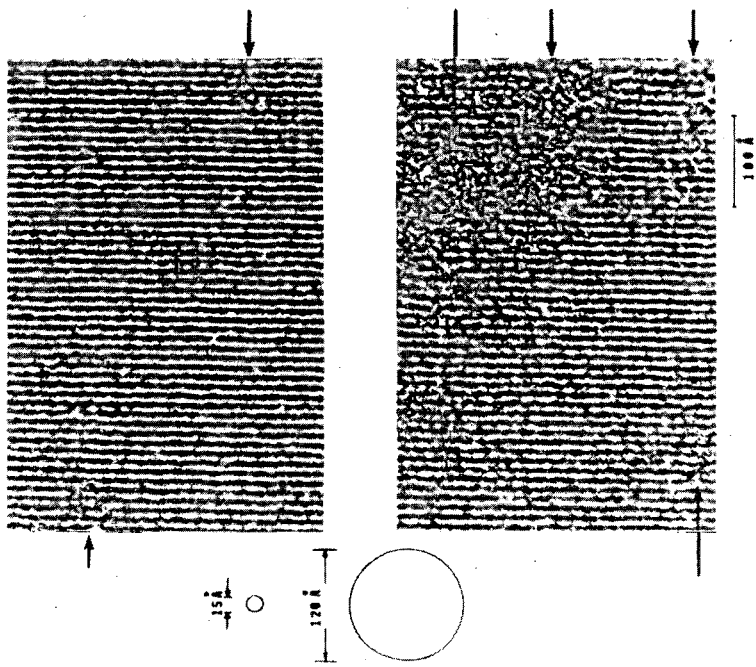
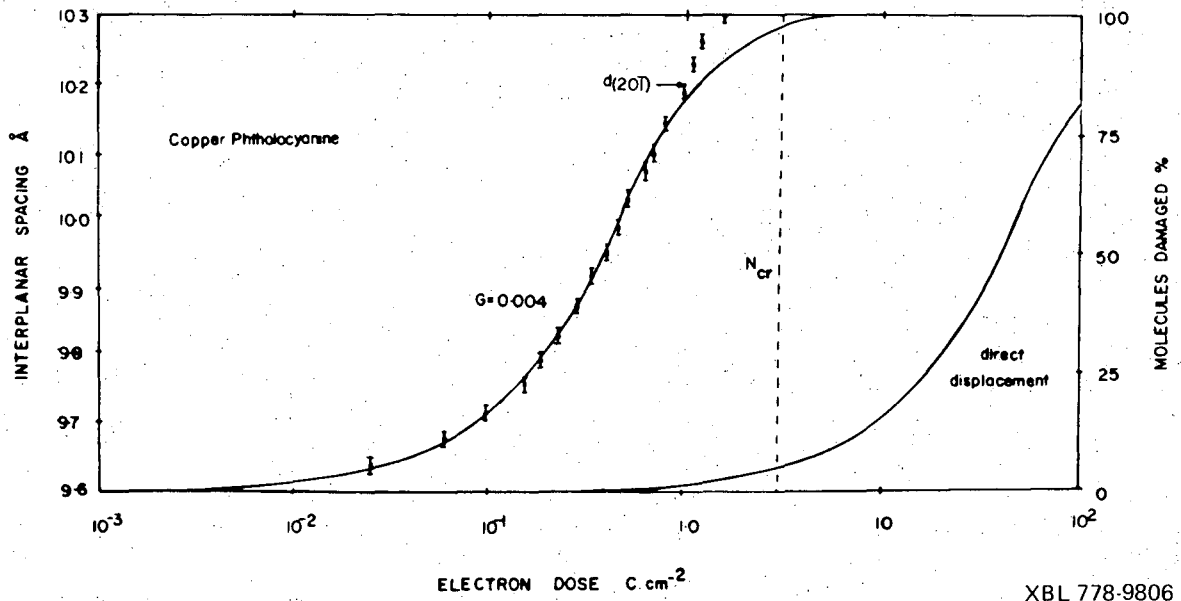
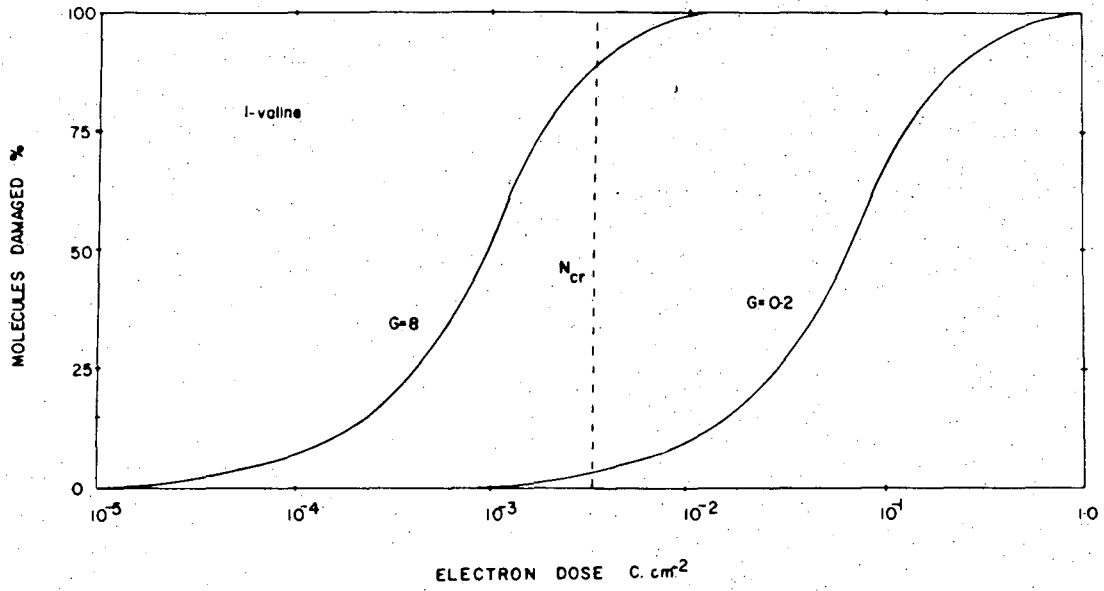


FIG. 3



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FIG. 4

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