Observation of screw dislocations in lamellar stacks of polyethylene and isotactic polystyrene

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Lamellar stacks of polyethylene and isotactic polystyrene crystals are investigated by dark-field electron microscopy and electron diffraction. The observed effects suggest the presence of screw dislocations, the Burgers vector of which is parallel to the chain direction. The dislocation density in lamellar stacks is greater than 10^{11} cm^{-2}. The occurrence of the dislocations is attributed primarily to shear forces arising from thermal stresses.

INTRODUCTION

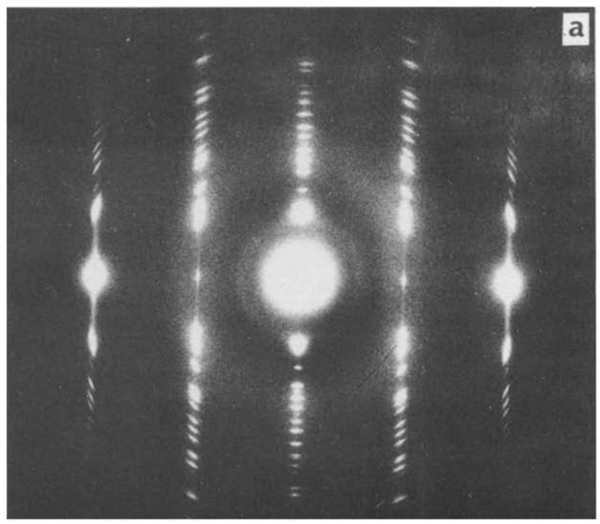
Defect structures in crystalline solids are of considerable interest in the understanding of their physical properties. Although many lattice defects have been proposed in macromolecular crystals[1], their direct observation by transmission electron microscopy is limited, due to experimental difficulties. The major difficulties arise from radiation damage of the crystals in the electron beam[2] and from the microscopic size of the crystals, creating problems in resolving their lattice defects. It is the purpose of this paper to report observations obtained by transmission electron microscopy suggesting the existence of screw dislocations resulting in a relative displacement of the chains along the chain direction.

EXPERIMENTAL PROCEDURES

The investigations were made on linear polyethylene (Alathon 7040) and isotactic polystyrene (from Polyscience Inc.). Electron transmitting films having a high uniaxial orientation were obtained following the procedure described elsewhere[3,4]. The films had a thickness of less than 1000Å. Under this condition, dynamical effects in scattering and image formation can be neglected[5]. The polyethylene films were annealed for two hours at 128°C and the polystyrene was crystallized for 20 minutes at 200°C. Investigations were made using electron diffraction and dark-field imaging. The microscope used was a Jeol JEM 200 A operated at 100 kV. Photographs were taken on high sensitive X-ray films, Agfa D 10.

RESULTS

Figures 1a and *b* show the electron diffraction pattern of highly oriented polyethylene and polystyrene films. In addition to the diffraction spots, fine streaks appear on the first and higher order layer lines. The streaks are situated



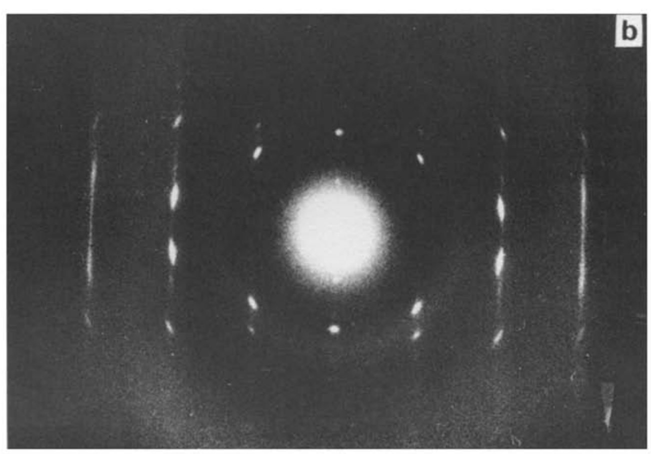


Figure 1 Electron diffraction pattern from highly oriented (a) polyethylene and (b) isotactic polystyrene

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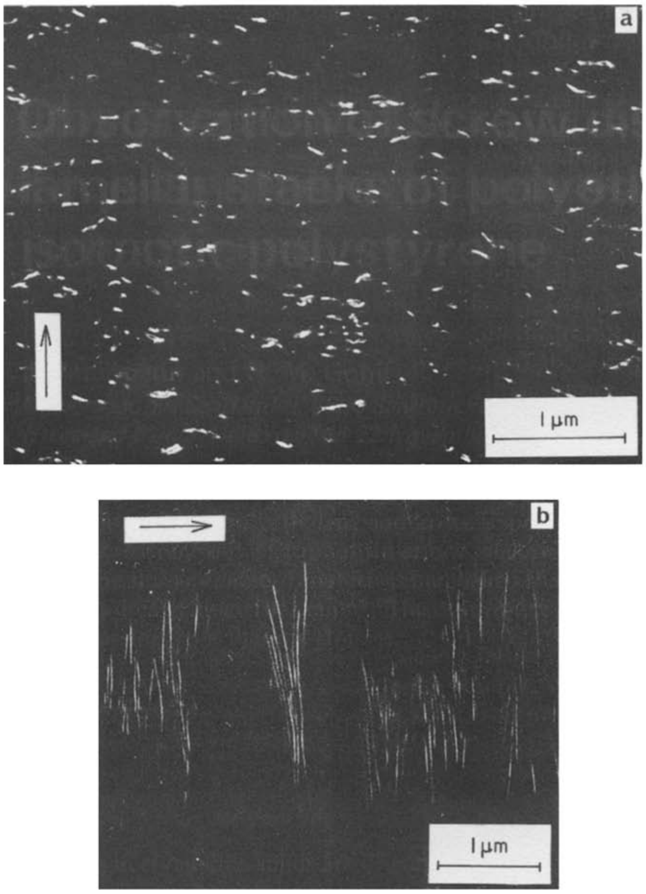

Figure 2 Dark-field electron micrographs of lamellar stacks in (a) polyethylene g = [110] and (b) isotactic polystyrene g = [220]

perpendicular to the molecular direction. The intensity of the streaks remains unchanged on rotating the samples about the [001] direction in the tilting stage of the microscope. *Figures 2a* and *b* are dark-field electron micrographs of polyethylene and polystyrene respectively taken using [110] and [220] spots for imaging. The uniform bright contrast from the lamellar crystals is due to their being in Bragg reflecting conditions with respect to the incident electron beam. When an [hkl] spot ($l \neq 0$) is used for imaging, a pattern of dark lines parallel to the molecular direction is visible in the crystalline lamellae (*Figures 3a* and *b*). The spacing of the line pattern is at the resolution limit of the micrographs. Similar results have also been obtained from oriented material after cold drawing and subsequent annealing or without heat treatment of melt crystallized fibres.

DISCUSSION

Three types of lattice defects can give rise to the observed diffraction pattern and dark-field observations:

(a) A fine dispersed second phase within the orthorhombic or trigonal lattice of the polyethylene or polystyrene lamellae, where the structure factors of the (hk0) planes for both the phases remain unaltered.

(b) Faults in the stacking sequence of the (001) planes with the structure factors of the (hk0) planes being unaltered by the fault displacements.

(c) Line defects parallel to the molecular direction, in which the structure factors of the (hk0) planes remains unchanged, for example screw dislocations with Burgers vectors b = [001].

For a finely dispersed second phase new spots in the diffraction pattern are expected which is not the case for both the polymers.

From the observations of streaks with the same intensity at any rotation angle about the molecular direction in the electron diffraction pattern, it can be concluded that the intensity distribution of an (hk0) spot in reciprocal space has the shape of a disc, the plane of which is normal to the molecular direction. The discs in the diffraction pattern can result from a two dimensional fault having the described features. In order to account for the rotational symmetry and the uniform intensity distribution on the streaks, any (hk0) plane must act as a habit plane of the fault and the distance of two fault planes must range from one lattice spacing to infinite.

On the other hand screw dislocations with the Burgers vectors parallel to chain direction (*Figure 4*) and with a sufficiently high dislocation density are also in accordance with the observed diffraction pattern and imaging conditions*. Usually a distinction between the two kinds of defects can easily be made by an analysis of the contrast profiles[7]. With having only a few hundred Angstrom thick lamellae, very close spacings of the faults, and the thickness of the sample being below the extinction distances[5], an evaluation of contrast profiles is difficult. From structural arguments it is hard to believe that stacking faults of the described kind can

* The intensity depleted zone close to the [hk0] reflection, as predicted by the theory[6], will be smeared due to the particle size broadening of the reflection.

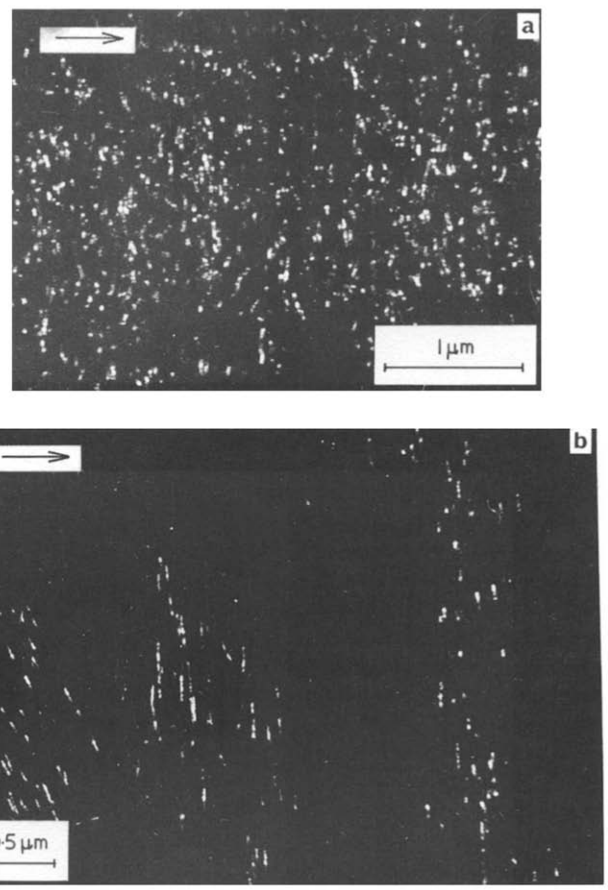

Figure 3 Dark-field electron micrographs (g = [hkl], $l \neq 0$) of lamellar stacks in (a) polyethylene g = [002] (b) isotactic polystyrene g = [012]

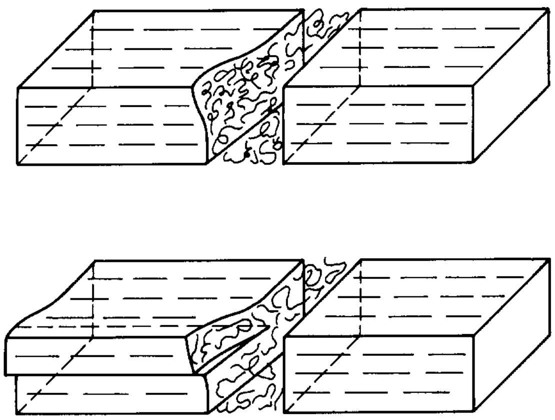

Figure 4 Schematic sketch of a screw dislocation in a crystalline lamellae

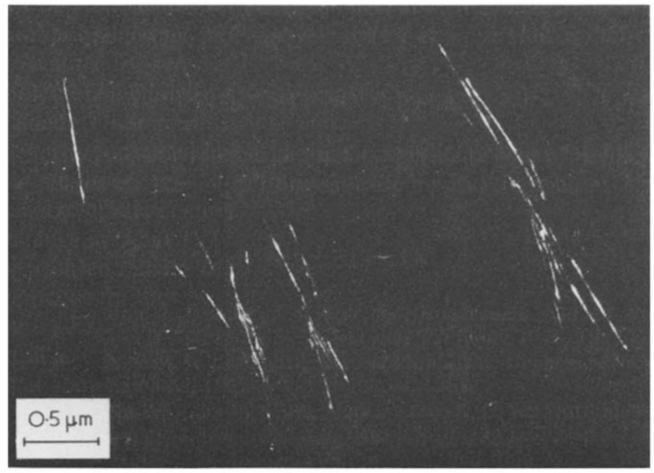

Figure 5 Dark-field electron micrographs (g = [012]) of isolated lamellae in isotactic polystyrene

be located at any ($hk0$) plane. Furthermore, overlapping and inclined fault planes are expected to be within the crystalline lamellae leading to a more uniform contrast than observed.

Screw dislocations responsible for shearing the crystal parallel to the chain direction have already been predicted and observed in polyethylene single crystal[8,9,10]. Our observation of the high dislocation density (about 10^{11} cm^{-2}) together with the rather straight lamellae imply that the sign of the Burgers vector (plus or minus) is random. Schultz and Kinlock[11] have developed a theory for the lamellar twisting in which the twist is created by sets of screw dislocations located in [$hk0$] planes. One set of the screw dislocations can be of those as described. According to their model, with the signs of the Burgers vectors alternating an oscillation of the lamellae around an [$hk0$] screw axis rather than a twist will occur. If we consider the structure depicted in *Figure 4*, thermal stresses due to the different thermal expansion coefficients between crystalline and amorphous material in connection with local fluctuations of the ratio d/l (d = crystalline thickness in chain direction, l = long period) will create shear stresses and can be responsible for the creation and existence of the dislocations, even in the annealed state.

Indeed, on reducing the interface stresses by separating the lamellae as is the case in strained hard elastic polyethylene fibres[12], the intensity of the streaks in the diffraction pattern decreases considerably. The comparatively low screw dislocation density in solution grown polyethylene single crystals[9], in which no shear stresses are present is in accordance with the above mentioned suggestion.

In isotactic polystyrene the influence of thermal stresses on the number of the line defects can be investigated more directly. In the case of lamellar stacks, as they exist in row structures[13], shear stresses resulting from the different thermal expansions of the amorphous and crystalline areas are more pronounced than within a single isolated lamella being totally surrounded by amorphous material. In the case of a lamella surrounded uniformly by amorphous material (*Figure 5*), different thermal expansion coefficients of the crystalline and amorphous phases will create compressive stresses rather than shear stresses. While shear stresses are necessary to create dislocations, the number of screw dislocations in isolated lamellae is expected to be smaller than in a stacked arrangement of lamellae. In polystyrene, where single lamellae can frequency be observed the number of screw dislocations is considerably smaller (*Figure 5*) than in lamellar stacks (*Figure 3b*). This observation is in accordance with our explanation that thermal stresses are responsible for the observed screw dislocations.

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