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Lattice Defects in Organic Crystals

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Since the last review of this topic at the 1969 Brookhaven Symposium the principal efforts in this area have been directed towards the characterization of both point and line defects and the preparation of low defect content samples for physical and chemical examination.

The techniques of surface microscopy and dislocation etching provide the simplest methods for assessing the dislocation content of the solid. Careful study of the size, shape and distributions of etch-pits can lead to the definition of the basic slip systems and their relative facility. A wide variety of solids have now been examined and the general applicability of the technique demonstrated. The results of some recent examinations of aromatic and linear-chain hydrocarbon solids will be outlined.

More recently, confirmation of these results has come from the related techniques of electron microscopy and x-ray topography. The former is the more powerful technique for the examination of dislocations and its high resolution permits the examination of highly defective systems in great detail. The recent achievements of Thomas and his coworkers in overcoming the problems of stability of organic solids in the electron beam will no doubt lead to the wider use of this method for chemical and physical studies. In spite of the lack of resolution of the x-ray topography technique it has the major advantage that for samples of low ($\leq 10^5 \text{ cm}^{-2}$) dislocation content, individual dislocations can be identified and characterized in the bulk crystal ($1 \times 1 \times 0.1 \text{ cm}^3$). Thus the geometry and propagation of dislocations in "as grown" crystals can be examined. Examples will be shown of the x-ray topographic examination of molecular solids and the complementary nature of the etching and topographic techniques.

One important extension of the utilization of these techniques is the examination of the propagation of dislocations in organic crystals during growth, the absolute perfection attainable and the influence of mechanical handling on the perfection of the crystal. An assessment has been made of the perfection of crystals grown from the melt, from the vapour phase and from solution.

For the first, crystals grown by the Bridgman technique are highly defective but growth by the Czochralski technique is much more promising. In vapour growth, the production of highly faceted crystals leads to improved perfection but mechanical damage which occurs on removal of the crystal from the substrate can be disastrous. By far the best specimens are obtainable by growth from solution. Here again however the ultimate perfection depends upon the properties of the dislocations.

Other than the single report on differential expansivity by Baughman and Turnbull which indicates that the dominant point defect in succinonitrile and cyclooctane will be a lattice vacancy, no further "direct" measurements of the concentrations and energetics of point defect formation have appeared. The probing of the nature and properties of these defects via self-diffusion studies has continued. The extension of these measurements to a wider range of molecular solids have emphasized the interference of diffusion along dislocations in the overall process and hence the necessity to characterise the specimens used. The basic measurements have been extended to mechanistic studies and both the pressure dependence and isotope-mass dependence of radiotracer self-diffusion strongly support previous speculations that the dominant, mobile, point defect in molecular solids is the lattice vacancy. The magnitudes of the diffusion coefficients obtained suggest that the concentrations of these defects will be similar to those found for other solid systems.