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Effects of Crystal Growth Environment on Defect Concentrations in Anthracene Crystals†

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Abstract—An efficient yet inexpensive crystal growing furnace has been constructed. With this furnace crystals have been grown with helium, argon, nitrogen or xenon as the inert gas heat exchanger. The nature of this inert gas affects the concentration of defects within the bulk of the crystal. Thus, though several crystal parameters are invariant under these conditions, this is not always the case, particularly at low temperatures. A low pressure of helium is found to have the least effect upon these crystal parameters.

1. Introduction

As interest concerning the properties of molecular crystals has grown, it has become obvious that " purity " of the experimental specimen is of fundamental importance. The term " purity " includes both chemical and structural parameters. Techniques for chemical purification of anthracene have been extensively studied,(1,2) and the preparation of high quality material is straightforward. However the effects of variations in crystal growth techniques on the structural defect distributions remains unknown except in general terms; e.g. differences between sublimation and melt-grown crystals.(3,4) Thus, though most studies are undertaken using melt-grown crystals, little attention has been paid to defining the optimum conditions for preparing these crystals. Consequently, we have recently designed and used a simple, efficient and inexpensive furnace which affords easy control over all of the principal crystal-growth parameters, and have found that crystals grown in this

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furnace are comparable to those grown in a more expensive and sophisticated electrical Bridgman furnace.(5)

As an initial investigation we have used this furnace to produce crystals under different inert gas atmospheres, and have measured and compared several experimental characteristics of these crystals, finding them to be markedly different in many instances.

2. Crystal Preparation

Purified Eastman X-480 anthracene was used as the starting material.(1) The inert gases used as the temperature exchange medium for the crystals were all of mass spectrograde quality. A mass spectrum analysis of these gases showed no evidence of any impurity which was considered to be active, i.e. oxygen, water vapour etc., and all were greater than 99.9% pure. Gas pressures were measured during the final sealing processes into the crystal growing tube following transfer of the anthracene charge from the zone refiner. Break seals were used throughout to ensure no contamination by air during any filling process. Inert gas pressures of between 0.1 cm and 60 cm of mercury(3,6,7) were used, with 30 cm pressure as a comparative standard. The crystal growing tubes were of equal size and shape. With the furnace employed for crystal growth, two crystals were grown simultaneously, under the same growth and annealing conditions. The design of the Bridgman furnace used is shown in Fig. 1. The low-temperature (lower) bath consisted of a 3-litre beaker containing silicone oil (710 Dow Corning), supported inside a 4-litre beaker which had its base cut off. The air gap between these two beakers was a sufficient barrier to inhibit significant thermal changes due to draughts etc. in view of the large bulk of the silicone oil. The main supply of heat to this lower bath was provided by a simple hot plate, used to bring the bath temperature to within 10 °C of that required. The final 10 °C was supplied by a low-wattage, wire heater, thermal regulation being achieved with an electronic relay and thermoregulator. This complete lower bath was supported on a Lab-Jack facilitating the adjustment of spacing between the upper and lower baths and giving easy access for inserting or removing a crystal tube. The upper bath (high temperature) consisted of three concentric pyrex tubes joined as

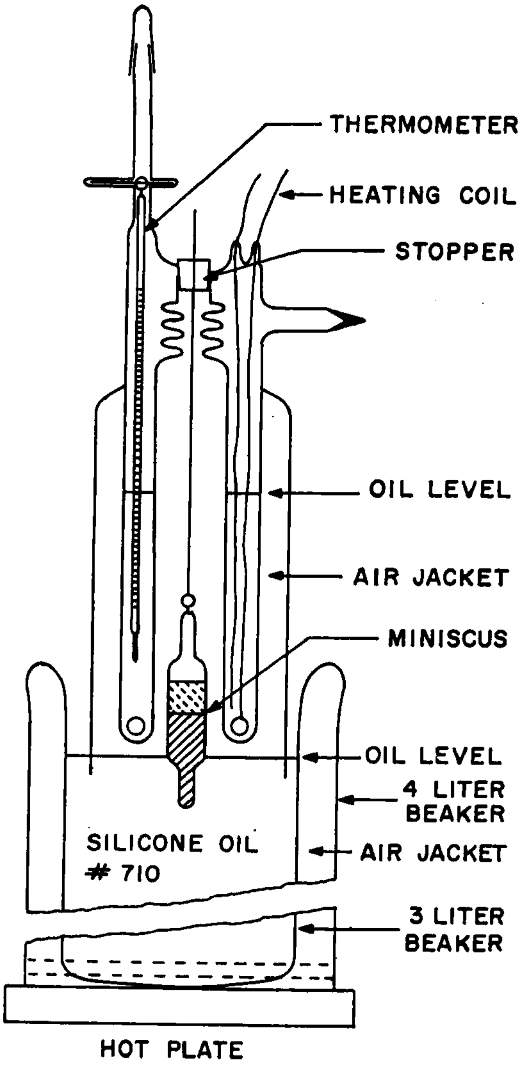

Figure 1. Schematic diagram of the crystal growing furnace.

shown in Fig. 1. Typical dimensions used for these tubes were 30 × 11 cm ID, 27 cm × 8 cm ID and 27 × 5.5 cm ID. Silicone oil (710 Dow Corning) was filled to a depth of ~20 cm in the centre cavity, and heated by a coil of resistance wire. Temperature control was obtained using a constant voltage regulator, the temperature being monitored by a thermocouple or directly with a thermometer. It was not necessary to seal the high temperature silicone oil from the air as is shown in the figure, although sealing inhibits the deterioration of the oil. We have used such a furnace continuously for longer than 6 months without any changes being necessary.

Typical parameters used to grow anthracene crystals were: Upper bath ~230 °C, lower bath ~208 °C, separation ~1 cm. A growth rate of ~0.1 cm/hr was satisfactory for crystals having a cross sectional area of ~1 cm^2. There are many obvious changes which would improve the performance of this furnace, including using vacuum jackets instead of air insulation, stirring the lower bath, etc., but the purpose of developing a simple furnace would then be defeated. We have studied the temperature stability and distribution of this furnace over a period of time using thermocouples and found it to be both stable and reproducible. To study the effects of changes of temperature gradient on crystal growth for example, it may be necessary to map the temperatures distribution to determine absolute values, but this is a simple process. It is important to note that the crystals produced have been found to be comparable (i.e. triplet lifetime, singlet lifetime, hole and electron trap density etc.), to those crystals produced in electric furnaces under similar growing parameters, providing highly purified starting materials are used. This simple furnace design offers many attractive features for producing melt-grown crystals; for example (1) the temperature of the two zones may be independently varied with little change in the uniformity of the temperature gradient, (2) the temperature gradient may be easily varied by raising or lowering the temperature of the lower bath, (3) the progress of crystal growth may be visually followed since the complete furnace is transparent, (4) as crystal growth proceeds the crystallized portion is held at a uniform temperature, and annealing is thus uniform, (5) simple changes, such as using cooling coils in the lower bath, can extend the temperature range of the furnace below room temperature, (6) inexpensive liquids, e.g. water, may be used provided they have a satisfactory temperature range.

3. Experimental Characteristics of Crystals Grown Under Different Inert Gases

The results which are recorded below were all observed on crystals which had been grown under inert atmospheres of ~30 cm Hg pressure, crystal diameter ~1 cm^2, and growth rate ~0.1 cm/hr. Mass spectrograph grade helium, nitrogen, argon and xenon were used as the heat exchange gas within the crystal growing tube. After growth was completed all crystals were slowly cooled to room temperature over a period of 2 days to ensure the removal of any annealable defects. Annealing at ~210 °C was found on occasion to effect even the visual quality of crystals grown under different conditions, for example a high growth rate, and hence was included in the preparative techniques for all crystals, though its effect is not known.

Single crystals ~2–3 mm thick were then cleaved $||\,ab$ plane from these ingots and used for the investigations.

(A) Triplet Lifetime

No systematic difference was observed for any series of crystals. The triplet lifetime varied between 20–25 msec depending upon the purity of the initial anthracene charge and the position in the ingot used to produce the crystals.(2,8) Room temperature triplet lifetimes from the same position in the ingots were approximately equal. The room temperature triplet lifetime was used as a final test to ensure that no change in bulk properties had occurred in the crystals during the other investigations.

(B) One-carrier Space Charge Limited Currents

Space charge limited electron and hole currents were injected individually into the crystals using solid injecting contacts. In all cases trapping was evident, being greater for holes than electrons. θ values(9) of $\sim 10^{-1} - 10^{-2}$ and $10^{-2} \rightarrow 10^{-4}$ were typical for electrons and holes respectively with applied fields of ~5000 V/cm. The current-voltage (I, V) relationship indicated that crystals grown under nitrogen or helium generally had the least trapping. This difference in trapping is much more evident in low temperature I, V measurements.(9)

(C) Double Injection Space Charge Limited Currents

The temperature dependence of double injection space charge limited currents showed evidence of more severe trapping in xenon or argon atmosphere crystals compared to those grown under helium. Figure 2 illustrates some typical results.(10) The current was always found to decrease with temperature. If conditions of thermal equilibrium are assumed (this is not strictly true), then these $J(V, T)$ measurements indicate shallow trapping levels of 0.2 eV in crystals grown under helium and deeper trapping levels in crystals grown under xenon. Crystals which showed the greatest difference between the predicted trap free current and the current observed, also showed the greatest current-temperature dependence. This J, T dependence increased as the inert gas was varied; from He, → N_2, → Ar, → Xe.

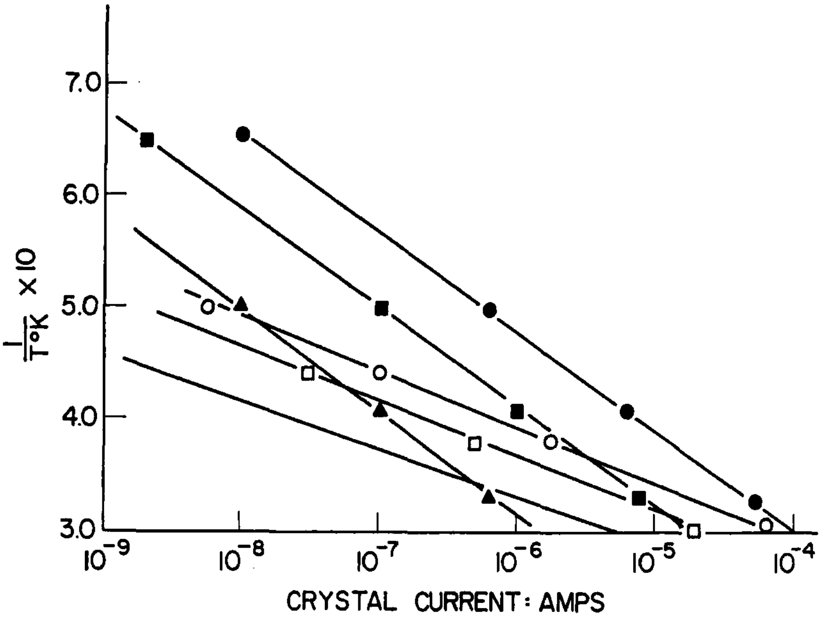

Figure 2. Temperature dependence of crystal current for crystals (2 mm thick) grown under helium (closed points) and xenon (open points). The voltages applied are ○ 2000 V, □ 1500 V and △ 1000 V.

(D) ELECTROLUMINESCENCE

Under conditions of double injection, electroluminescence was always observed emanating from these crystals. The same linear relationship between the electroluminescence intensity and the crystal current was observed, for all crystals and for temperatures between 150–350 °K.(11)

The electroluminescence spectra for crystals obtained with any specific exchange gas were selfconsistent, but considerable variance in the intensity of a broad structureless background emission was found between crystals of differing growth atmospheres, particularly at low temperatures. Figures 3 and 4 show the electro-

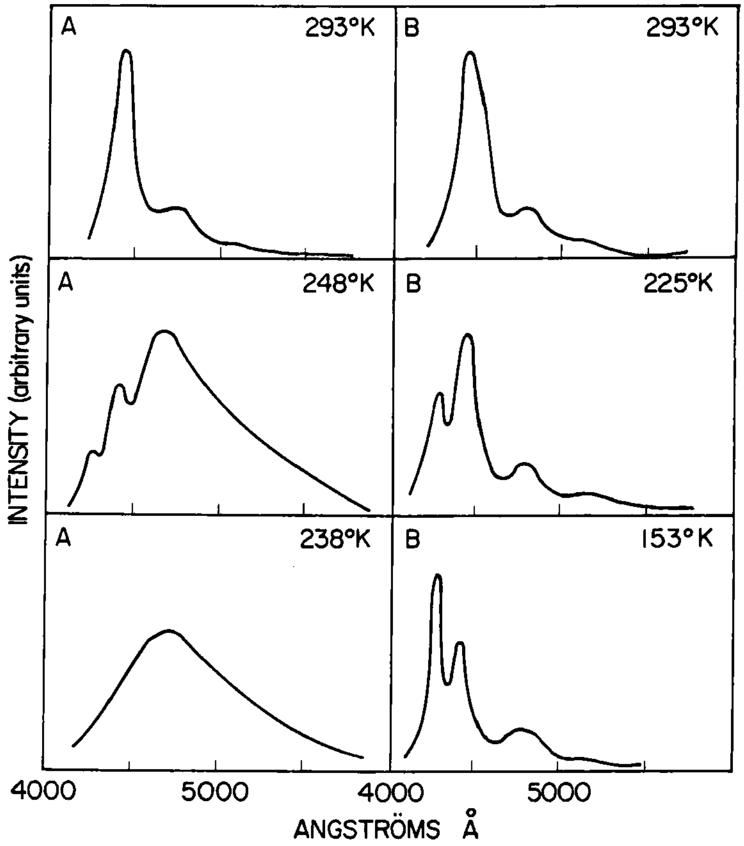

Figure 3. Electroluminescence Spectra observed for crystals grown under (A) xenon, (B) helium. Crystal current 10^{-6} amp cm^{-2}.

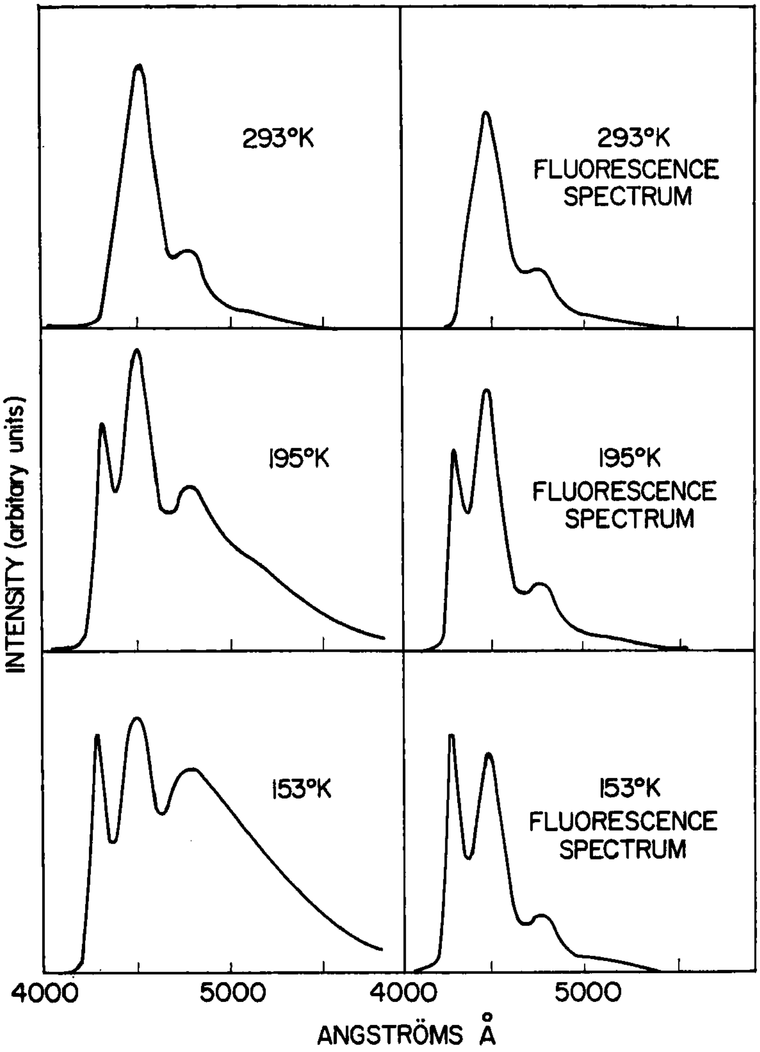

Figure 4. Electroluminescence Spectra and Fluorescence Spectra observed for crystals grown under argon. Crystal current 10^{-6} amp cm^{-2}.

luminescence spectra for crystals grown under He, Ar, and Xe. The optically excited fluorescence spectra for all crystals were identical. It was apparent that defect electroluminescence emission appeared at progressively higher temperatures as the inert gas was changed from helium → nitrogen → argon → xenon. This gradation is presumably due to a progressive increase in the density of either hole or electron traps, which then act as recombination sites.

(E) FLUORESCENCE EMISSION

A background emission emanating from either eximers or defects is normally observed in fluorescence spectra from melt grown crystals at low temperatures, $\sim 4\,^{\circ}\mathrm{K}$.(12) If the sharp line fluorescence spectra of a typical sublimation flake is subtracted from the fluorescence spectra of melt grown crystals, a structureless broad emission comparable to that observed for electroluminescence is obtained. This indicates that similar sites are involved in this region of the spectra, although electroluminescence is a much more sensitive probe due to excitation selectivity caused by carrier trapping. As would be expected, the dependence of low temperature fluorescence background defect emission on crystal growth parallels that observed for electroluminescence. Experiments have also shown that the radiative lifetime of this defect region of the spectra, $\{\lambda > 5000\,\text{Å}\}$ is ~ 15 nsec compared to ~ 6 nsec for unperturbed anthracene emission.(12) Reabsorption is not involved in this comparison, since at these very low temperatures ($\sim 4\,^{\circ}\mathrm{K}$), reabsorption may be neglected.

(F) MASS SPECTROMETER ANALYSIS OF OCCLUDED GAS

Three factors could account for the differing number of defects caused by growing the crystals in different inert gas atmospheres: (i) increasing gas solubility in the crystal with increasing atomic weight, (ii) each occluded gas molecule could cause a larger number of physical defects in the crystal as the atomic volume of the gas increases (it should be noted that the experiments indicate the density of defects increase as the molecular weight and atomic volume of the gas increase), or (iii) impurity concentrations in the inert gases increase in the same manner as (ii).

Though it is not possible to completely rule out (iii), the gases used were of the highest mass spectrograde quality available, and the published analysis of these gases gives no indication that impurities should play an important role. Thus a mass spectrometer analysis was made of the occluded gas for a series of crystals. A typical analysis was performed as follows. Two ingots, 1 $cm^2 \times 2$ cm, grown under helium and xenon, respectively, were weighed and carefully sealed into a glass ampoule provided with a break-off seal. This ampoule had previously been carefully heat and vacuum treated for degassing purposes. The ampoule was then connected to a mass spectrometer and evacuated. The crystals were then carefully melted in an oil bath, releasing dissolved gases. The mass spectrometer connection was then re-evacuated to $\sim 10^{-7}$ mm, and the break-off seal was cracked. The evolved gas was then analysed by sweeping the mass spectrometer successively between the mass peaks of He → Xe → He → Xe. In this manner the effect of pumping on these gases could be eliminated. The results showed that the crystals contained a concentration of $\sim 10^{-7}$ moles of helium and $\sim 10^{-8}$ moles of xenon. Thus although helium effects the bulk properties of the crystals the least, it has a greater solubility in the crystal. Each xenon molecule therefore is able to affect the anthracene lattice to a much greater extent(13) than a molecule of helium.

(G) Dislocation Content

Under stringent conditions which ensured that no excessive strain was placed on the crystal, a comparison was made of the etch pit concentration on the (001) surfaces of crystals grown under helium and argon.(14) Oleum was used as the etchant.(15) Low- and high-magnification photographs of the etched crystal faces are shown in Figs. 5 and 6. The low-magnification photographs show the general distribution of individual and aligned dislocation etch pits to advantage whereas the high magnification photographs enable the concentration of etch pits at non-basal dislocations to be obtained. The total non-basal dislocation content was found to be comparable, and in agreement with other estimations in melt-grown crystals. However, there is a striking difference between the crystals, namely the high concentration of low angle grain boundaries prevalent in crystals grown under argon.

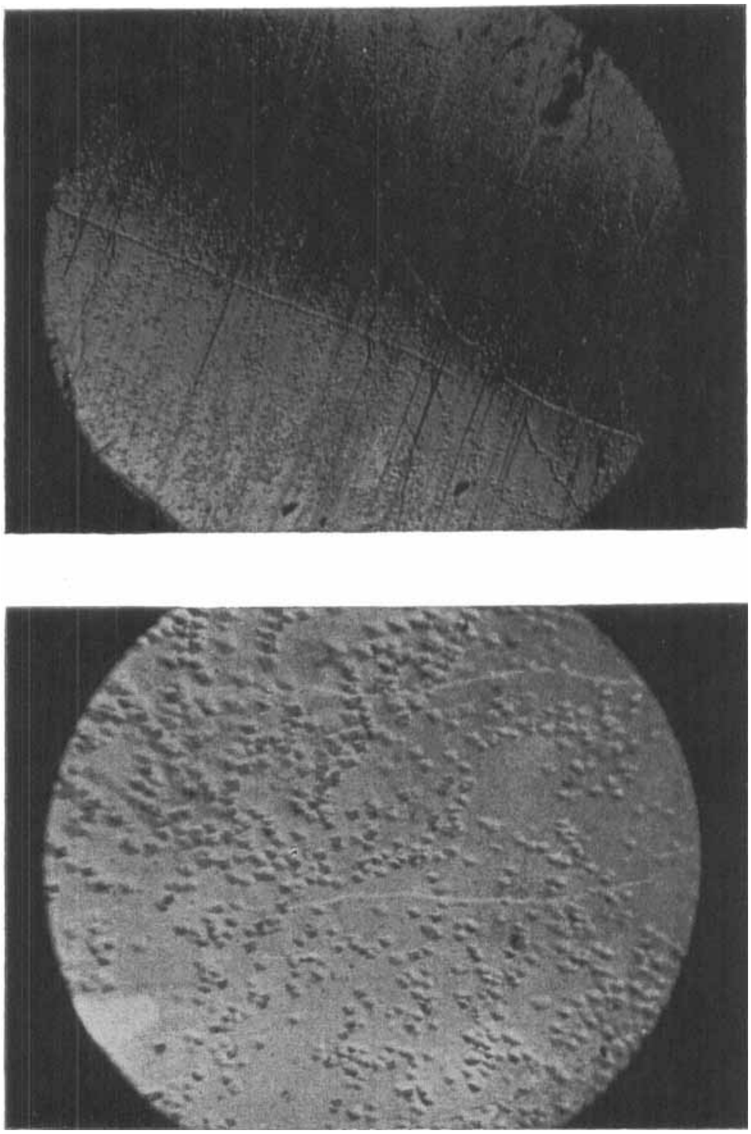

Figure 5. Low and high magnification photographs of the etch pit distribution on the (001) face of an anthracene crystal grown under helium gas. (Top ×210; bottom ×850.)

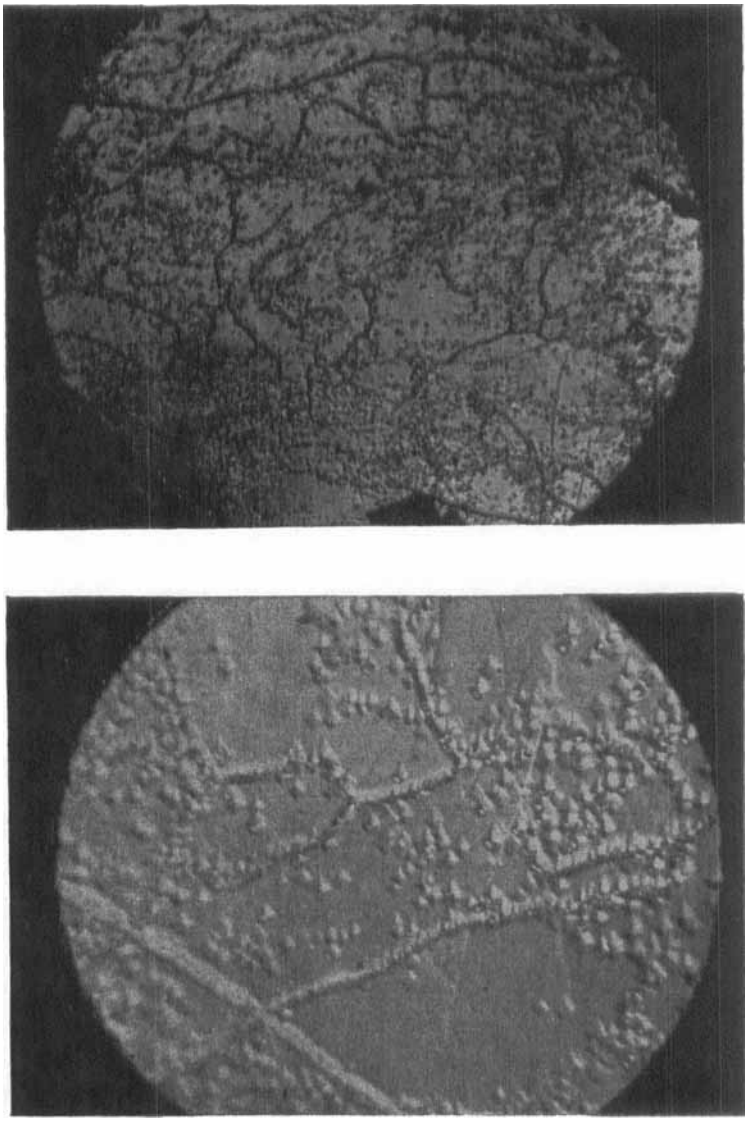

Figure 6. Low and high magnification photographs of the etch pit distribution on the (001) face of an anthracene crystal grown under argon gas. (Top × 210; bottom × 850.)

4. Conclusions

The characteristics of the inert gas used as a heat exchanger in producing melt grown crystals are not unimportant. The density of inert gas molecules within an anthracene ingot produced under typical growing conditions ($\sim 1 \rightarrow 100$ mm gas pressure) is of the same order of magnitude as the density of carrier traps determined from SCL current measurements $\sim 10^{15}$–10^{16} cm^{-3} although these two parameters may or may not be related. Comparative experiments have shown that the nature of the heat exchanger gas can significantly effect the results of observations concerning bulk properties of anthracene crystals, particularly at low temperatures. In general, the least effect on crystal parameters is found if helium is used as the heat exchange medium and its pressure is kept as low as physically possible, e.g. less than 1 mm mercury.

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