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THE INFLUENCE OF LATTICE IMPERFECTIONS
ON THE CHEMICAL REACTIVITY OF SOLIDS

THE GROWTH AND PERFECTION OF
TNT SINGLE CRYSTALS

by

John N. Sherwood
Hugh G. Gallagher

FINAL REPORT

FEBRUARY 1984

United States Army
EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY
London England

CONTRACT NUMBER DAJA-37-81-M-0395

Professor John N. Sherwood
University of Strathclyde

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Influence of Lattice Imperfections on the Chemical Reactivity of Solids.		5. TYPE OF REPORT & PERIOD COVERED FINAL TECHNICAL
7. AUTHOR(s) J.N. Sherwood		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Strathclyde Department of Pure and Applied Chemistry Glasgow G1 1XL, Scotland.		8. CONTRACT OR GRANT NUMBER(s) DAJA37-81-M-0395
11. CONTROLLING OFFICE NAME AND ADDRESS USARDSG (UK) Box 65 FPO, New York 09510		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 6.11.02A 1T16 1102BH57-02
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC		12. REPORT DATE FEBRUARY 1984
		13. NUMBER OF PAGES 33
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Limited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) TNT, Single crystals, Crystal growth, Crystal perfection, Dislocations, Morphology, Polymorphism, Twinning.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report presents an assessment of the purification and preparation of large perfect single crystals of TNT. In the course of this examination, studies were made of the polymorphism of this material and the influence of impurities on growth twinning. The defect structure of the best crystals was defined using X-ray topographic techniques.		

SUMMARY

This contract forms a direct continuation of the work initiated on contract DAERO-78-G-078 into the nature of the defect structure of organic energetic materials. The basis of, and background to, the work involved in the study as a whole is given in the introduction to the final report on that contract. In DAERO-78-G-078 a full and complete examination was made of the crystal growth and the nature and behaviour of growth defects in PETN and RDX with some supplementary work on other materials (Nitroguanadine, HMX, DATB and TATB). The period of the present extension has been devoted to the definition of the conditions for the growth of large single crystals of Trinitro-toluene (TNT) and the analysis of the crystallographic and defect structure of this material.

TNT proved to be a very difficult material to prepare in single crystalline form. This was due principally to the low purity of the material and the potential ease with which the readily incorporated impurity caused twinning to occur in the lattice. The structural consequences of the twinning were defined and the influence of impurity on twinning was examined.

This information was used to develop methods to prepare ultra-pure and highly perfect specimens of single crystals of this material. In these the nature and propagation of growth defects were defined.

These results are summarized in the following report. Fuller details are available in the Doctoral Thesis of H.G. Gallagher (University of Strathclyde, 1984).

KEYWORDS: TNT, Single crystals, Crystal growth, Crystal perfection, Dislocations, Morphology, Polymorphism, Twinning.

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1. INTRODUCTION

In order to investigate the defect structure of crystals of 2,4,6-trinitrotoluene (TNT) by the technique of X-ray topography, it is necessary to grow fairly large crystals of reasonable perfection and of known crystallographic structure. Although the crystallization behaviour of TNT has been the subject of considerable interest in the past, there is still a great deal of confusion regarding the structure of the crystallization products, and the conditions under which they are obtained.

Large crystals (up to 2cm in size) have been grown by the method of precipitant infusion [1]. Examination by Berg-Barrett topography revealed these crystals to be of comparatively poor quality, with local misorientations of one to two degrees. The Berg-Barrett method can be used without accurate knowledge of crystal structure, which was not defined for the crystals used in this study. Only limited information can be obtained by this technique and individual defects were not imaged.

The structural aspect of the crystallization of this material has been extensively studied by various authors using X-ray diffraction techniques [2-11]. Calorimetric methods have been used to investigate the thermal behaviour of the solid [12,13]. Although it has been shown to be complex, several conclusions can be reached regarding the crystallographic nature of TNT:

1. TNT can exist in at least two polymorphic forms and possibly several variants in each structure. The basic polymorphs have monoclinic and orthorhombic structure.
2. Both forms are stable under ambient conditions for long periods and undergo a transformation of one phase to the other at a definite temperature.

3. Both polymorphs can be prepared at ambient temperature and under different conditions of crystallization and, in particular, from different solvents.
4. Twinning has been noted by several authors.

The results of various workers on crystallization from solution are often conflicting, however; crystallization from a particular solvent yielding an orthorhombic polymorph for some workers and the monoclinic form for others.

The purpose of the present work is to define more exactly the structural nature of the products of crystallization of TNT from various solvents and to determine the most appropriate solvent for the growth of large, highly perfect crystals suitable for study by X-ray topography.

2. EXPERIMENTAL

2.1 Crystal Growth

Crystals of TNT were grown from saturated solutions by solvent evaporation at room temperature (Ca. 293K). A range of organic solvents was used, namely methanol, ethanol, cyclohexanol, toluene, acetone and ethyl acetate. The rate of crystallization was controlled by altering the rate of solvent evaporation.

Spontaneous nucleation yielded crystals of good optical quality from all solvents with the exception of ethyl acetate. This solvent formed solutions which were supersaturated to a high degree, and once nucleated, crystallised rapidly producing crystals of poor quality. Seeding of this solution prevented the build up of large supersaturations and resulted in the growth of crystals of greater perfection.

Ethyl acetate was selected as the most appropriate solvent for the growth of large single crystals by temperature lowering methods (See section 3.6). Slow cooling of seeded solutions at the rate of 0.01K hr^{-1} in the temperature range 303-309K was employed.

The crude material was purified before use in crystal growth by the method of Gey, Dalbey and Van Dolah[14]. TNT as supplied was orange/brown in colour, which became straw coloured after treatment by this method.

Crystal morphology was determined by measurement of interfacial angles using a Wooster two-circle goniometer and comparison with calculated angles for the unit cell described by Duke [10].

2.2 Polymorphism

The structural nature of the crystallization products from each solvent was assessed using powder diffraction methods. A number of crystals from each growth run were selected and ground to a fine powder. Diffraction data were obtained with a Guinier focussing camera using molybdenum ($\lambda K_{\alpha 1} = 0.709\text{\AA}$) and chromium ($\lambda K_{\alpha 1} = 2.289\text{\AA}$) radiation. Patterns were recorded on Ilford Industrial G film.

Rotation and zero-layer Weissenberg photographs were made using a crystal obtained from ethyl acetate solution. The crystal selected had a plate-like habit with approximate dimensions $2.0 \times 2.0 \times 0.5\text{mm}^3$. The crystal was mounted with the camera axis normal to the large face of the crystal. Diffraction data were recorded on Ilford Industrial G film using Mo K radiation.

The thermal behaviour of powdered samples of this material was studied using a Du Pont differential scanning calorimeter.

2.3 Twinning

Twinning was investigated using Laue diffraction techniques. Laue patterns were obtained using both copper radiation from a conventional X-ray generator and the synchrotron radiation source (SRS) at the Daresbury Laboratory, Daresbury. The SRS can be used in two modes. With a pin-hole collimator, a Laue pattern is produced which (neglecting small differences due to differing beam characteristics) essentially resembles that from a conventional source. Alternatively, using a larger collimator (maximum diameter 2cm) a Laue pattern is produced in which each spot is a topographic image of the crystal[15]. Laue diffraction patterns were recorded on Agfa Osray M3 film while using the laboratory X-ray source and high resolution Agfa Structurix D2 film at the SRS.

2.4 X-Ray Topography

Crystal perfection was assessed using X-ray topography. Transmission X-ray topographs were made using $\text{CuK}_{\alpha 1}$ radiation and were recorded on Agfa Structurix D4 film. The $20\bar{4}$ reflection was used in all cases.

A crystal grown from ethyl acetate by slow cooling was sectioned using a solvent saw with toluene as the cutting solvent. Both this crystal slice and complete crystals grown from other solvents were washed in toluene before topographic examination. This removed surface damage which may have been introduced during handling. The sample thickness was approximately 1.5mm, giving a $\mu_0 t$ value of 1.1.

3. RESULTS AND DISCUSSION

3.1 Crystal Growth

Growth by solvent evaporation produced crystals of optically good quality, in which typical size and colour varied considerably with solvent. It was found, however, that generally the size of the crystals obtained from each solvent increased as the solubility of TNT in the solvent increased. From cyclohexanol (~1% solubility) needle-like crystals, 2mm in the largest dimension, were obtained. Whereas platey crystals produced from toluene solution (~55% solubility) were typically 10x10x2mm³ in size, although crystals up to 20 x 20 x 3mm³ were grown. The maximum thickness achieved for any crystal was 4mm.

Crystals grown from alcohol or acetone were varying shades of amber, whilst those obtained from toluene and ethyl acetate were coloured yellow and faintly yellow respectively.

Slow cooling from ethyl acetate solution produced crystals of high optical quality up to 47x10x3mm³ and 2.5g in weight. Typical growth times were of the order of 2-3 weeks.

The crystallization data for TNT are summarised in Table 1.

3.2 Polymorphism

The structural nature of a selection of crystals grown from each organic solvent was assessed by powder diffraction techniques. For all the samples examined, only two types of diffraction pattern were obtained, depending on the solvent from which the crystals were grown. These patterns are shown in Figure 1*. Pattern A was obtained by growth from cyclohexanol and ethanol solutions, whilst pattern B was produced by crystallization from the remaining

solvents. The type of pattern was found to be independent of the supersaturation of the growth solution. Crystals obtained from a particular solvent by growth at different rates always produced the same pattern. The calculated values for d-spacings are given in Table 2. Both patterns are very similar, although a number of lines missing in one pattern are present in the other and vice-versa. These patterns are consistent with those obtained previously [12] which were assigned to the monoclinic and orthorhombic structures of TNT. Here, it is likely that the two patterns correspond to the two polymorphs identified before. Pattern A is attributed to the orthorhombic form and pattern B to the monoclinic phase.

The structure of a crystal grown from ethyl acetate solution (powder pattern B) was determined using rotation and zero-layer Weissenberg methods. Analysis of diffraction data revealed this crystal to be monoclinic with unit cell dimensions $a = 21.23\text{\AA}$, $b = 6.10\text{\AA}$, $c = 15.02\text{\AA}$ and $\beta = 110.72^\circ$. This cell is consistent with that already obtained by other workers [9, 10] and confirms that specimens which exhibit powder pattern B are indeed monoclinic. Splitting of many diffraction spots, due to twinning, was noted. However, diffraction images resulting from twinning were ignored in the measurement of unit cell dimensions.

* Powder diffraction experiments were carried out using both copper $K_{\alpha 1}$ ($\lambda = 1.54\text{\AA}$) and chromium $K_{\alpha 1}$ ($\lambda = 2.289\text{\AA}$) radiation. The higher wavelength radiation gives rise to a larger separation between the lines, and a corresponding reduction in their number, on the

pattern. Although some detail at lower d-spacings is missing, the major differences between the two patterns occur at higher values of d-spacing and consequently powder patterns produced using chromium radiation have been used to illustrate these differences more clearly.

3.3 Thermal Behaviour

When TNT of the monoclinic structure (powder pattern B, grown from methanol) was heated, its calorimetric trace recorded only the melting endotherm at a temperature of 354K. However, when the temperature of the orthorhombic form (powder pattern A, grown from cyclohexanol) was raised to melting, a second small endotherm ($\Delta H_{\text{trans}} = 0.22 \text{ Kcal/mole}$) appeared at a temperature of 343K. After a period of two months, further samples from the same batch were run. What had previously yielded two endotherms now produced only a single melting endotherm, identical to that observed for the monoclinic polymorph. The DSC traces are given in Figure 2.

The absence of any endotherms up to melting for monoclinic TNT suggests that this form is stable from ambient temperature (Ca. 293K) to the melting point. The appearance of a second endotherm upon heating of the orthorhombic form indicates that this polymorph undergoes a well-defined transformation to another polymorphic form (probably the monoclinic form) at a temperature around 343K. This, together with the fact that the orthorhombic to monoclinic transformation also takes place at ambient temperature over long periods of time suggests that the orthorhombic form is metastable under ambient conditions. This type of thermal behaviour is similar to that observed previously [12, 13], with the values obtained for ΔH_{trans} in close agreement.

3.4 Twinning

Laue patterns were run of crystals of monoclinic structure using both a conventional X-ray source with copper radiation and the synchrotron radiation source. With the incident beam normal to the large plate face of the crystal, two types of pattern were obtained. The diffraction geometry is illustrated in Figure 3a and the resulting patterns are shown in Figures 4a and 4b. The first type, observed for crystals grown from all solvents (cyclohexanol produces orthorhombic crystals and is not included in this discussion) contained two mirror planes and one two-fold axis of rotation, i.e. Laue symmetry $2/m$. The second type, which was observed for only a small number of crystals grown from ethyl acetate solution, exhibited only mirror symmetry, i.e. Laue symmetry m . For monoclinic TNT the crystal space group and point group are $P2_1/c$ (according to Duke[10]) and $2/m$ respectively. Friedel's law reduces the point group to the centrosymmetrical point group m , which is the highest symmetry expected for this class. Laue symmetry $2/m$ is more typical of the orthorhombic structure. The apparent increase in symmetry from m to $2/m$ arises from twinning during growth by the stacking of alternate layers of monoclinic structure, each layer being rotated through an angle of 180° around the normal to (100) with respect to the adjacent one.

Typical full crystal Laue patterns of both twinned and untwinned crystals grown from ethyl acetate solution are shown in Figure 5. Both patterns were indexed using Duke's unit cell (Figure 6).

Most, though not all, of the spots in Figure 5a occur in pairs: one spot for each twin orientation. Along [001] the spot separation is greatest and each twin is almost imaged separately. As [010] is approached, the amount of overlap of the twin images increases until finally, along [010], the two images are superimposed and a topographic image of the whole crystal is obtained. Thus by appropriate selection of reflection, it is possible to investigate the defect structure in the twinned portions of the crystal, as well as in the whole crystal. Single spots which occur along other directions are due to the systematic absence of the nearby twin orientation reflection.

The dimensions of the twinned layers were investigated by orientating the crystal so that the (100) face was parallel to the incident X-ray beam. The diffraction geometry is shown in Figure 3b and an example of a topograph taken in this way is shown in Figure 7 for a crystal grown from methanol solution. There are several layers of various sizes up to a maximum of approximately 1mm. These layers arise from regions of the crystal in one twin orientation. The volumes between the layers are due to twin lamellae in the other orientation, which give rise to diffracted intensity elsewhere on the plate. Only crystals grown from ethyl acetate can be obtained in millimetre dimensions free from twinning.

The random nature of the twinning, occurring during the growth process, suggests that it takes place as a result of growth accidents. The material used here, although purified, still retains a relatively high impurity content. The presence of impurities in twinned crystals is confirmed by the observation of impurity related defects in many X-ray topographs (See section 3.6).

The role of impurities in twinning during growth is widely recognised. Two competing factors operate during growth: the desire to maximise density of packing and to adopt the highest possible symmetry.

Energetically, the difference in packing due to twinning must be small, otherwise it would never occur. The presence of impurities may reduce the small energy difference to such an extent that the dominant factor becomes the attainment of higher symmetry. Under these circumstances, the twin may form, mimicking the symmetry of the higher order orthorhombic structure. Once twinning has taken place, the crystal will grow in the new orientation until similar conditions prevail again. Here the crystal will adopt the original orientation and proceed to grow as before. This process of twinning followed by de-twinning, and so on, can continue as long as the necessary impurity is present, to give a crystal consisting of a series of twin lamellae stacked on top of one another. Twinning of the type observed here is unlike anything described previously in the literature for TNT.

Crystals grown from ethanol solution produced Laue patterns corresponding to both the twinned monoclinic structure and a third type of Laue pattern. This pattern is shown in Figure 4c. In comparison to the previous patterns, the spot asterism is larger, indicating a higher degree of strain within the crystal. Twinning is also evidenced by the occurrence of the diffraction spots in pairs. This twinning is different to that described above. Both these factors contribute to making unambiguous determination of the Laue symmetry more difficult. However, it is almost certainly

symmetry 2/m. This Laue symmetry can be derived from the space group obtained previously [10,11] for the orthorhombic form of TNT. The twinning in this case is probably that described by Carper and Davis [11].

3.5 Morphology and Habit

The morphology and habit of the monoclinic polymorph was studied. The crystal forms $\{100\}$, $\{102\}$, $\{001\}$, $\{10\bar{1}\}$, $\{10\bar{2}\}$, $\{30\bar{2}\}$, $\{110\}$, $\{011\}$, $\{1\bar{1}\bar{1}\}$, $\{111\}$ were observed with $\{100\}$ dominant. This is in agreement with the habit faces predicted from reticular area calculations, the results of which are given in Table 3. Variations in crystal habit with changes in growth conditions are attributed to the small differences in reticular area for forms other than $\{100\}$. Three types of habit, tabular, rod-like and acicular, were observed with increasing supersaturation, corresponding to a decrease in importance of the $\{100\}$ form and increasing elongation along $[010]$. All three habits are shown in Figure 8. Crystals grown at lower supersaturations, nearer to equilibrium growth conditions, exhibited well developed $\{100\}$ faces and consequently had a plate-like habit. Crystals of each habit were observed to grow in the same crystallizing dish. This is due to localised variations in supersaturation. Changes due to solvent were also observed. Crystals grown from ethyl acetate were longer along $[001]$ and showed well formed $\{011\}$, $\{1\bar{1}1\}$ and $\{111\}$ faces. This gives crystals grown from this solvent their characteristic coffin-like habit (Figure 9). Crystals grown from other solutions also exhibited these forms but to a much lesser extent. The typical morphology for a crystal grown from ethyl acetate by slow cooling is shown in Figure 10.

Crystals with the orthorhombic structure had a habit similar to that observed for the monoclinic structure. Crystals obtained from cyclohexanol were acicular in habit, often occurring as inter-woven needles. Ethanol grown crystals were generally tabular in habit, although rods and needles were also observed.

As the morphology of a crystal is dominated by its crystal packing, the similarity in habit reflects the similar crystal structures for the two polymorphic forms.

The presence of twinning cannot be determined conclusively by measurement of interfacial angles alone. In general, twinned crystals exhibit a more symmetrical habit than untwinned crystals. Figure 9 illustrates the differences between twinned and untwinned crystals. All crystals contain a mirror plane of symmetry normal to $[010]$. However, the untwinned crystals have a greater degree of asymmetry along $[001]$ when compared to the twinned crystals. In some cases, twinning results in a second mirror plane normal to this direction. Crystals with higher symmetry have a crystal habit more typical of that expected for a crystal with orthorhombic structure. However, the presence of twinning cannot always be detected from crystal habit alone. For the commonly observed faces of the untwinned crystal there exists a corresponding twin facet, with the same orientation and of similar morphological importance. This is easily understood by consideration of the stereographic projections plotted for the twinned and untwinned crystals. In Figure 11a the ten most commonly observed faces are plotted for the untwinned crystal. By carrying out the twinning symmetry operation a second stereogram is produced (Figure 11b). The habit faces of the twins

are labelled according to their own crystallographic axes and plotted as a cross (X) and open circle (O) respectively. Twinning gives rise to a second set of poles superimposed directly onto those of the untwinned crystal. Whether a given facet belongs to a twinned or untwinned crystal cannot be determined solely by goniometry. X-ray diffraction is required to identify twinning in this material.

3.6 Assessment of Crystal Perfection

The variation in perfection of crystals grown from different solvents was assessed by X-ray topography. This is illustrated in Figures 12-14 for crystals grown by solvent evaporation from methanol, toluene and ethyl acetate solutions.

The crystals shown in Figures 12 and 13, grown from methanol and toluene respectively, are highly defective and individual defects cannot be resolved. The high degree of strain within the lattice gives rise to large regions of the crystal which are out of contrast (white areas). Figure 14 shows a crystal grown from ethyl acetate solution under similar conditions. Crystals grown from this solvent are of much greater perfection than those obtained from other solvents. Most of the defects normally associated with solution grown crystals are observed: growth sector boundaries (G.S.), growth banding (G.B.), solvent inclusion (I) and dislocations (D). The greater quality of crystals obtained from ethyl acetate makes this solvent more suitable for the growth of larger crystals by temperature lowering methods.

The more accurate control of growth conditions achieved by slow cooling of seeded solutions of ethyl acetate resulted in a further improvement in crystal quality. Figure 15 shows a topograph of a section taken from a crystal grown in this way. The most notable feature is the influence of impurities on the 'grown-in' defect structure of this crystal.

The lateral growth sectors are highly imperfect, in contrast to the end growth sectors which contain a very much lower defect density. The inclusion of solvent predominantly into the $\{110\}$ growth sectors can be seen from the many small holes produced by polishing the crystal slice in preparation for topography. Solvent inclusions can also be observed lying along the growth sector boundaries.

Minor fluctuations in growth conditions leads to variations in impurity incorporation. This causes local changes in lattice parameters and gives rise to band contrast in the topographic image. These regions of varying impurity content are known as growth bands (G.B.) and occur normal to the growth direction.

Dislocations (D) emanate from the seed (S) or from solvent inclusions (I) and propagate normal to or almost normal to the growing crystal face. Upon crossing a growth band, the line direction of several dislocations is altered slightly. A growing dislocation will follow the direction of minimum line energy [16] which will normally remain constant for a given growth sector and Burgers vector. Local modification of the lattice parameters by impurities will give a new direction of minimum energy and consequently the dislocation deviates from its original path as it crosses the growth band.

The trace of the growth sector boundary is observed to lie along changing directions. The course of the growth sector boundary is defined by the growth rates of the faces separated by it. Under conditions of constant growth rate the boundary will follow a straight line. It has been shown already that the crystal morphology is sensitive to the changes in supersaturation which occur under different conditions of growth. With increasing supersaturation the rate of growth along [010] compared to [001] increases. The growth sector boundary grows along an irregular path due to variations in the relative growth rate of the competing faces along these directions. Changes in growth rate are caused by fluctuations in supersaturation during growth.

4. CONCLUSIONS

Both polymorphs of TNT can be prepared by crystallization from different solvents. Growth from cyclohexanol solution yields crystals of the orthorhombic phase, whilst the monoclinic form crystallizes from the remaining solvents. Both polymorphs have been obtained from ethanol solution.

The monoclinic structure is the stable polymorphic form from ambient temperature to the melting point. The orthorhombic phase is metastable at ambient temperature, but undergoes a phase transformation to the monoclinic form upon heating at a temperature of 343K. The orthorhombic to monoclinic transformation also takes place at room temperature over long periods of time.

In almost all cases, the monoclinic crystals exhibit twinning. Each crystal is made up of monoclinic layers stacked parallel to one another, each layer being rotated through an angle of 180° around the normal to (100) with respect to the adjacent one. The dimensions of the twinned layers normal to (100) are variable, up to a size of 1 mm. Only those crystals grown from ethyl acetate can be obtained in millimetre dimensions free of twinning. Twinning was also noted for the orthorhombic form.

Growth by solvent evaporation produces crystals in which typical size and colour varied considerably with solvent. For the monoclinic form, variations in crystal habit were observed with changes in supersaturation and solvent, although crystal morphology remained the same. The {100} form was found to be dominant, in agreement with reticular area calculations. The variations in habit with changes in growth conditions are attributed to the small difference in reticular areas for forms other than {100}.

Crystals grown from ethyl acetate were of greater perfection than those obtained from other solvents. Growth by temperature lowering yielded crystals of better quality than those produced by solvent evaporation.

Crystals grown from ethyl acetate solution by slow cooling were found to be both large in size and highly perfect. They have the monoclinic structure and can be grown free from twinning. This makes crystals grown from this solvent most suitable for a detailed investigation of the defect structure of TNT by X-ray topography.

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SOLVENT	HABIT*	SIZE/mm ³	COLOUR	POLYMORPH ⁺	TWINNED ⁺⁺
ETHYLACETATE	COFFIN-LIKE	47 x 10 x 3	FAINT YELLOW	MONOCLINIC	YES AND NO
METHANOL	ND. RD. PL.	5 x 4 x 1	DARK AMBER	MONOCLINIC	YES
TOLUENE	PL.	10 x 10 x 2	YELLOW	MONOCLINIC	YES
ACETONE	ND. RD. PL.	5 x 4 x 1	AMBER	MONOCLINIC	YES
ETHANOL	ND. RD. PL.	2 x 1 x 0.25	AMBER	MONOCLINIC AND ORTHORHOMBIC	YES
CYCLOHEXANOL	ND.	2 x 0.5 x 0.5	AMBER	ORTHORHOMBIC	YES

* ND. = Needles; RD. = Rods; PL. = Plates

⁺ See section 3.2

⁺⁺ See section 3.4

Table 1: CRYSTALLISATION DATA FOR TNT

<u>Line Number</u>	<u>Pattern A</u>	<u>Pattern B</u>
1	7.00	7.06
2	5.63	5.62
3	5.42	-
4	-	5.22
5	5.01	4.99
6	4.92	-
7	-	4.75
8	-	4.58
9	4.30	-
10	4.29	4.28
11	3.91	4.03
12	3.89	3.89
13	-	3.85
14	3.76	3.77
15	3.69	3.67
16	3.54	3.53
17	3.44	3.48
18	3.34	3.39
19	3.27	3.29
20	3.17	3.16
21	-	3.11
22	3.05	3.02
23	3.01	2.96
24	-	2.93
25	2.88	2.86

Table 2: Calculated d-spacings for two types of powder pattern

Morphological Importance	Form h,k,l	Reticular Area
1	100	2.46
2	102	6.55
3	001	6.98
4	$10\bar{1}$	7.01
5	$10\bar{2}$	8.17
6	$30\bar{2}$	8.23
7	110	8.44
8	011	8.80
9	$1\bar{1}\bar{1}$	8.81
10	111	9.46

Table 3: Calculated reticular areas for forms h,k,l
in order of morphological importance.

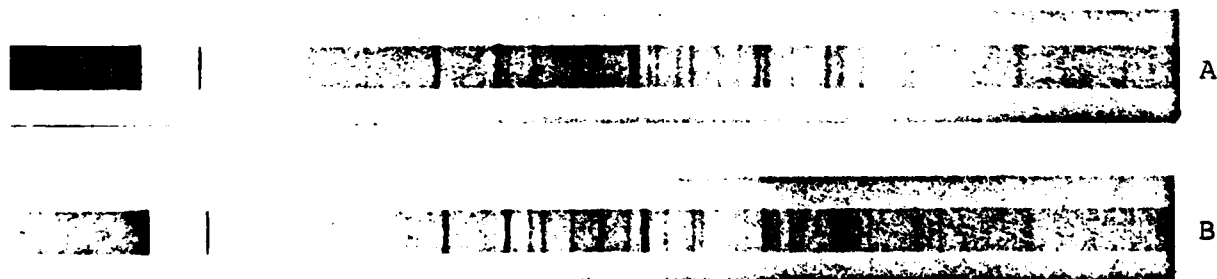


Figure 1: TNT powder patterns

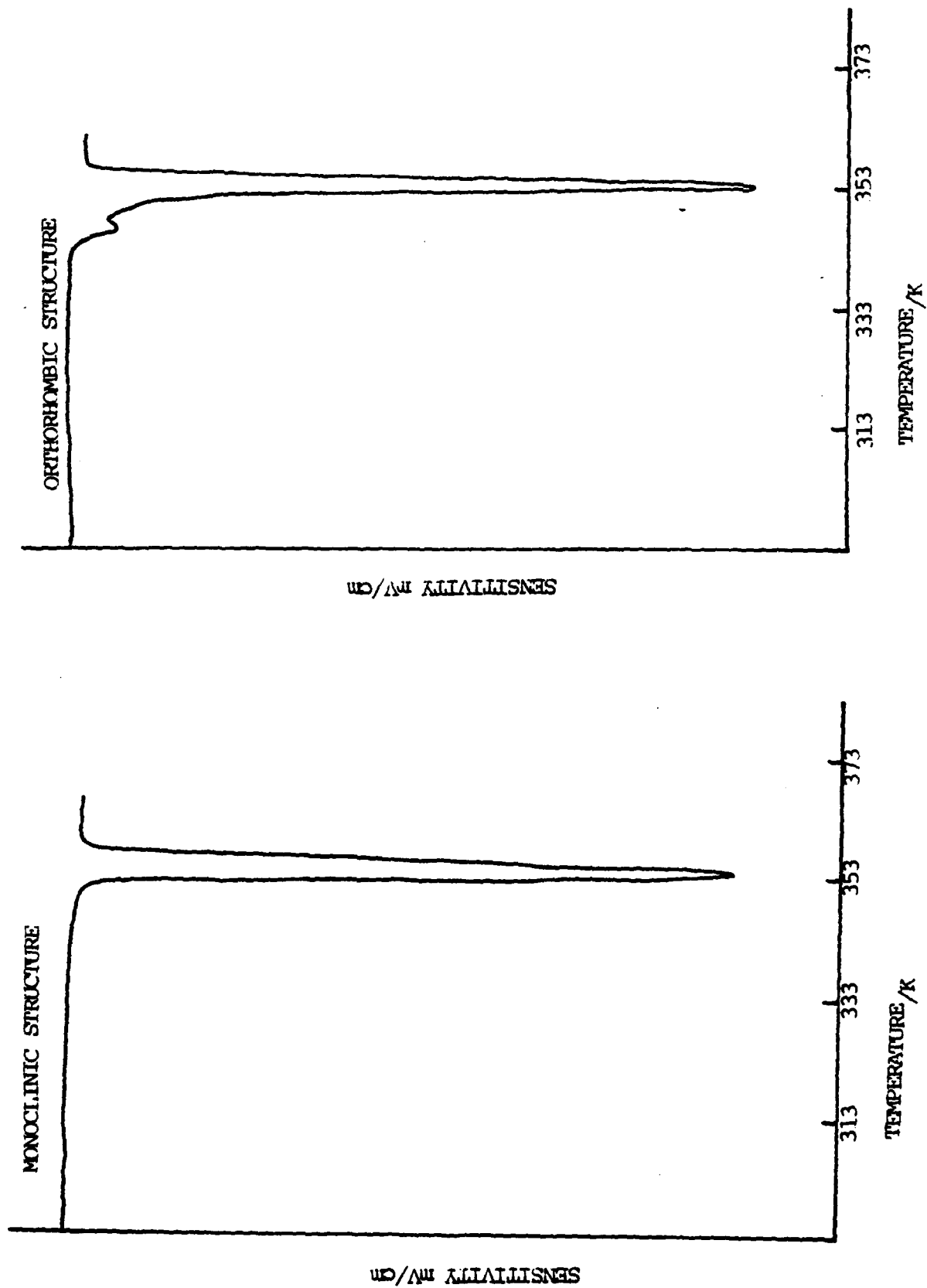
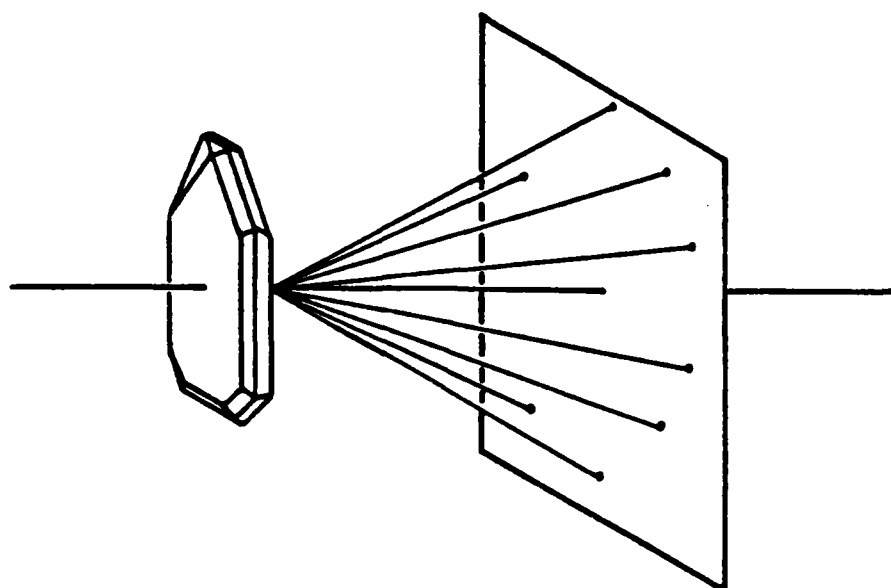
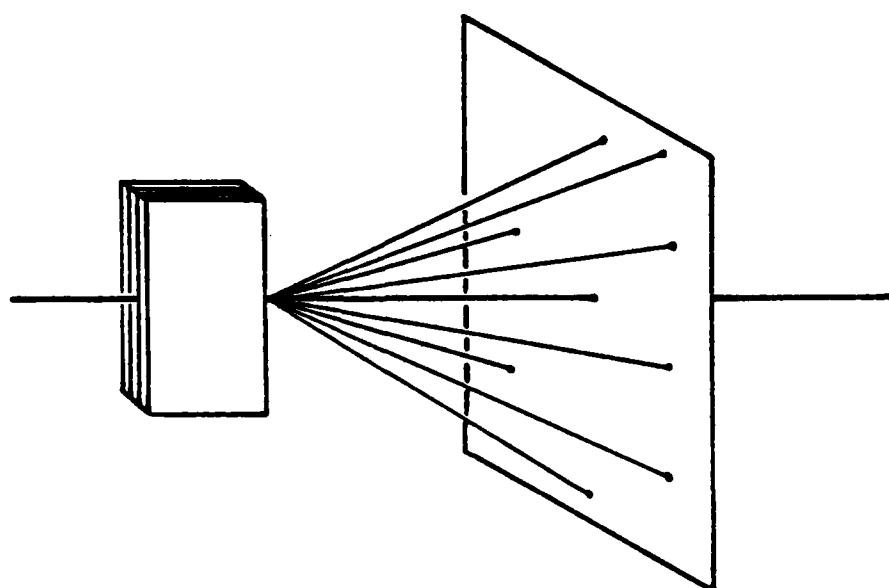


Figure 2: D.S.C. traces for T.N.T.



a) Investigation of crystal symmetry.



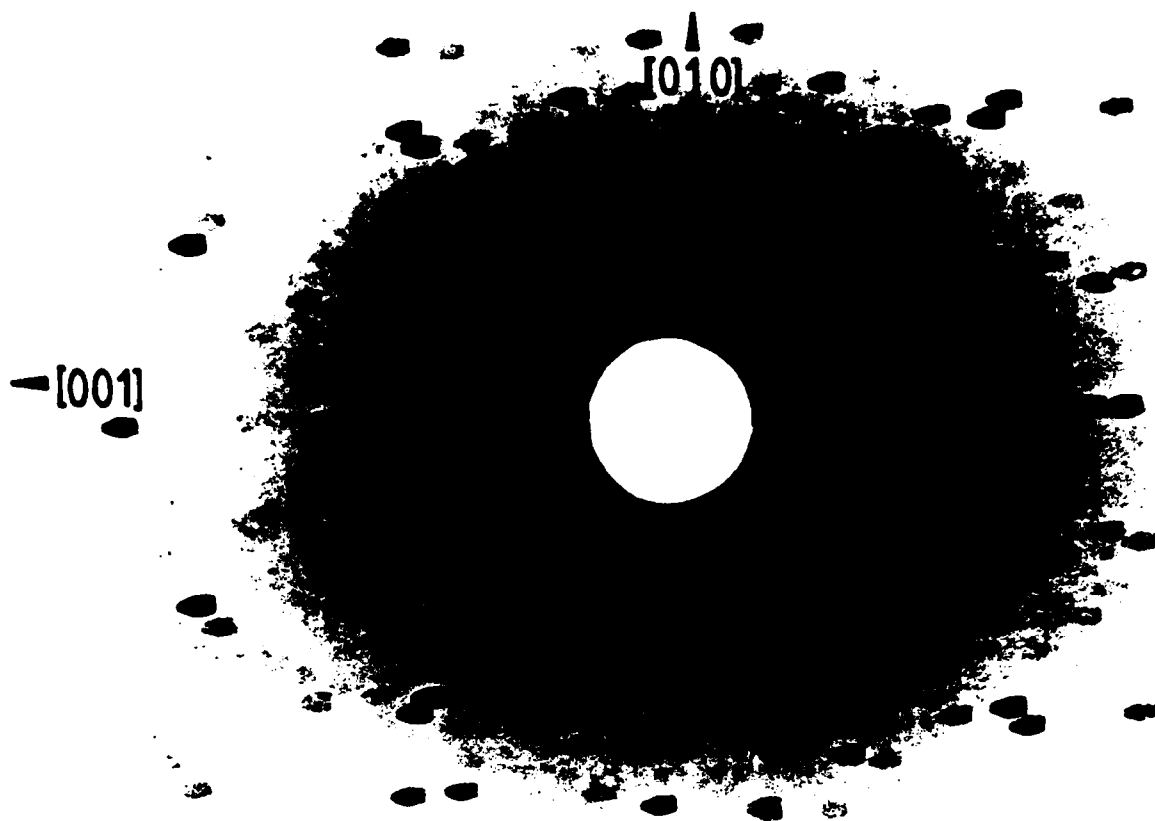
b) Investigation of layer structure.

Figure 3: Laue diffraction geometry.

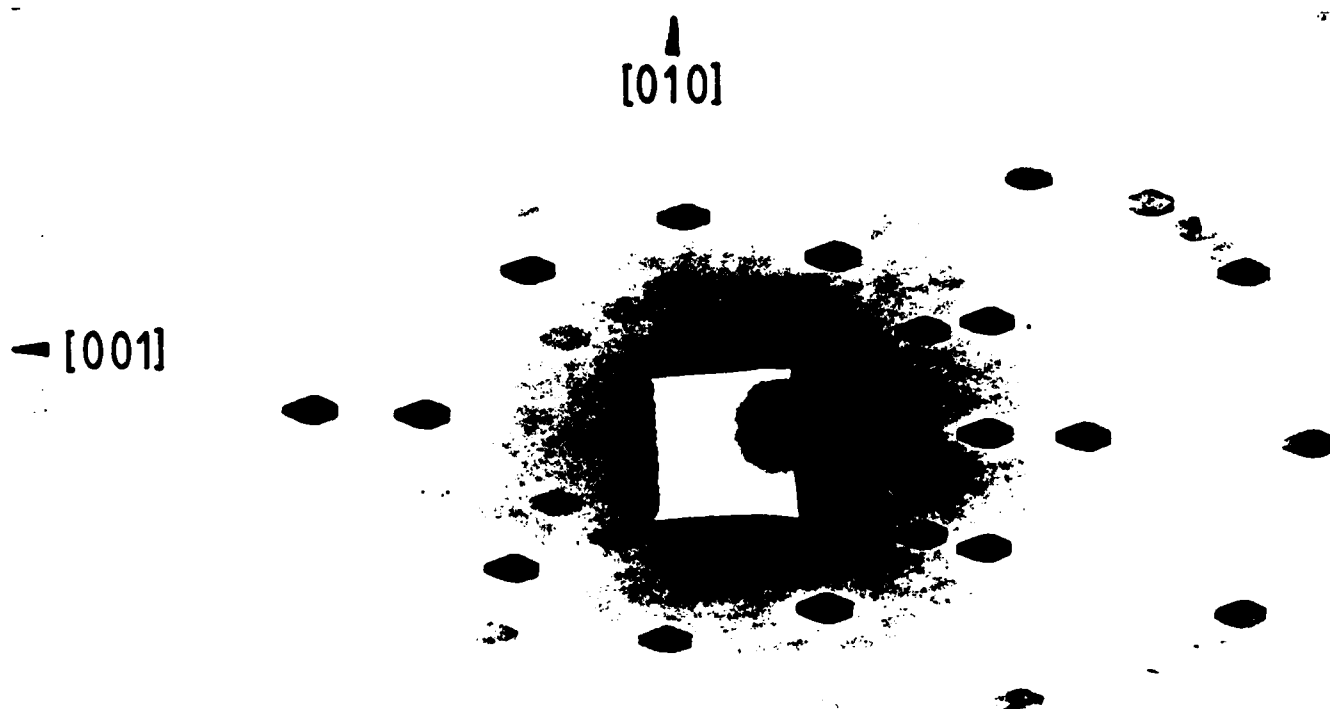


a) monoclinic, twinned crystal b) monoclinic, untwinned crystal c) orthorhombic, twinned crystal

Figure 4: TNT conventional transmission Laue patterns (spec-film distance 3cm)

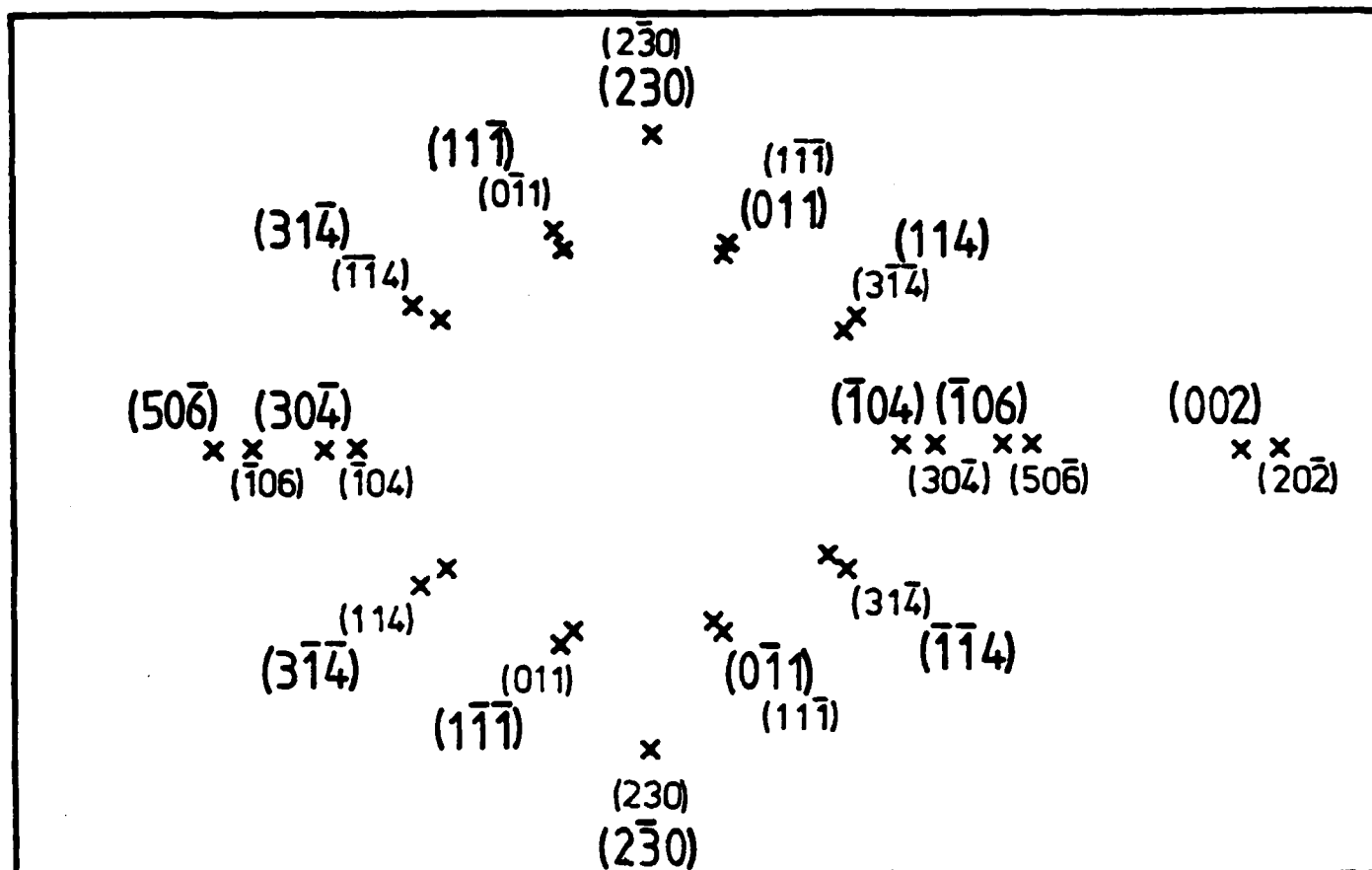


a) Twinned crystal

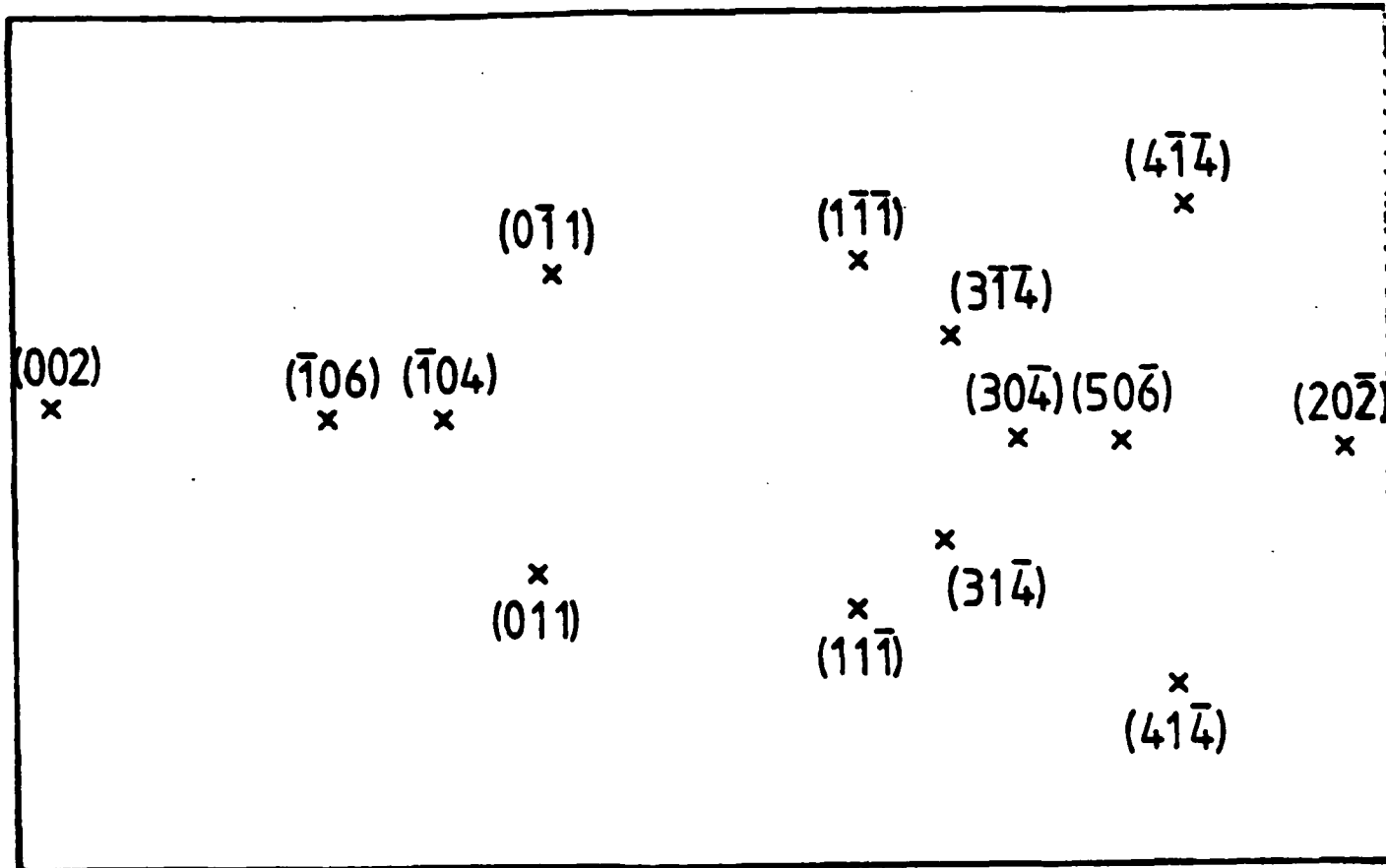


b) Untwinned crystal

Figure 5: SRS topographs transmission Laue geometry
(spec-film distance 10cm)

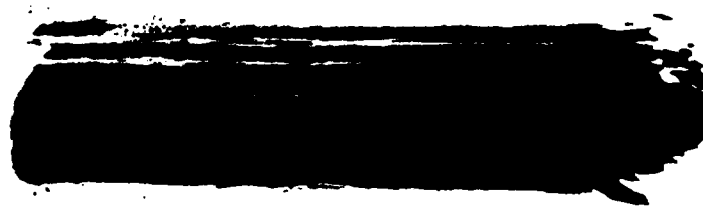


a) Twinned crystal



b) Untwinned crystal

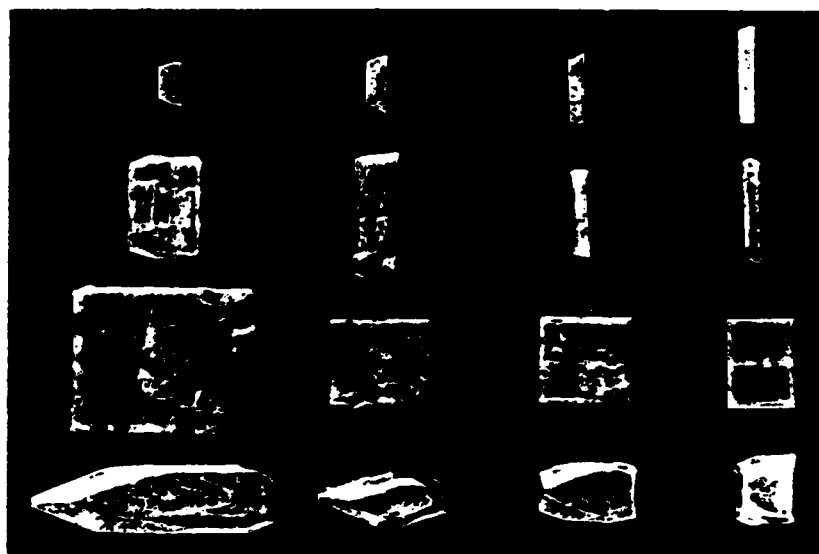
Figure 6: Indexed Laue patterns



Scale mark 1mm

g →

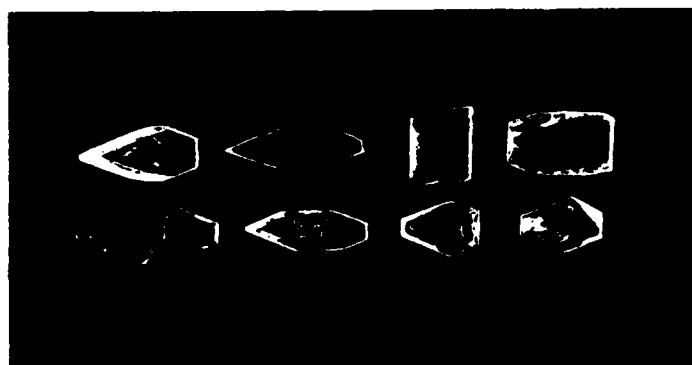
Figure 7: Topograph showing twin layer structure.



Scale mark 1mm

Increasing supersaturation →

Figure 8: Variation in habit with supersaturation.

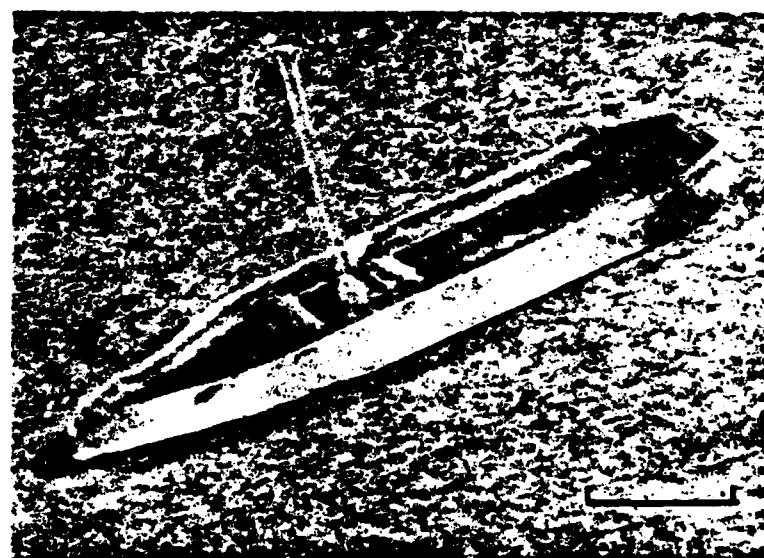
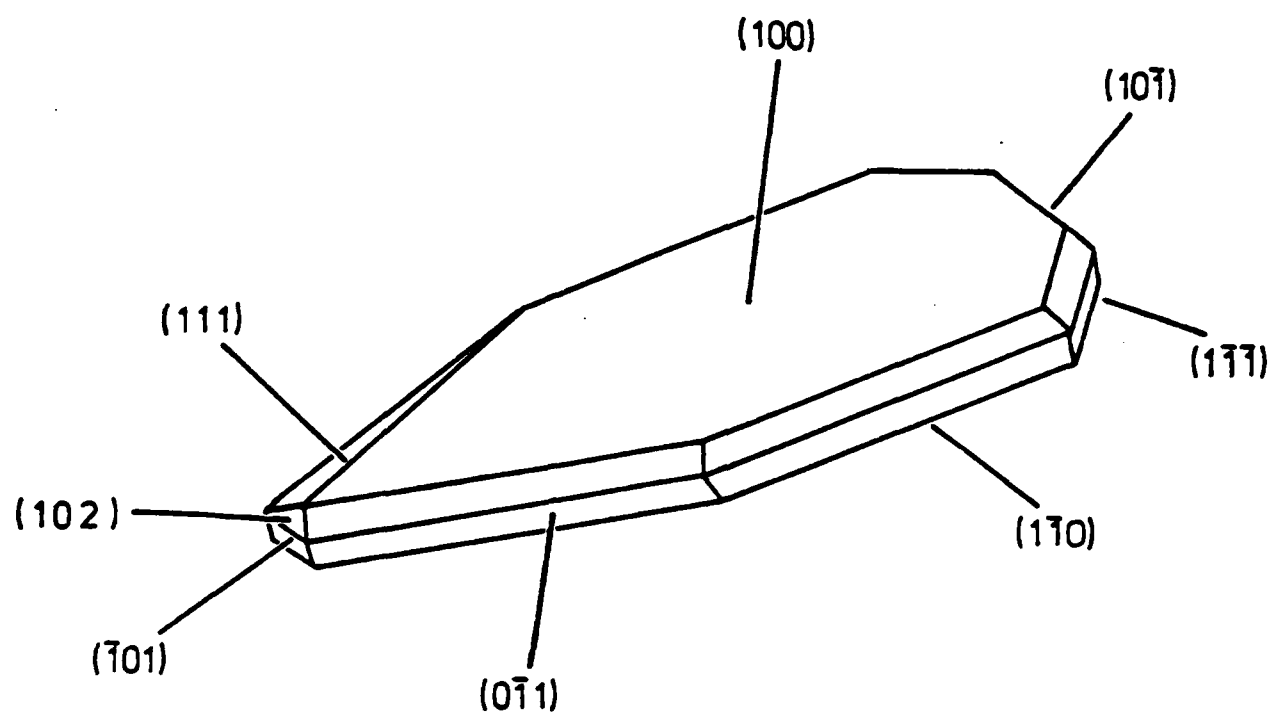


Scale mark 1mm

Untwinned

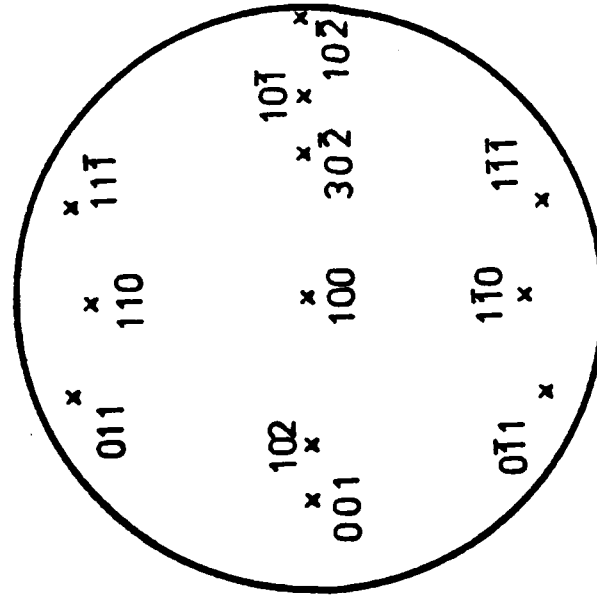
Twinned

Figure 9: Crystals grown from ethyl acetate solution.

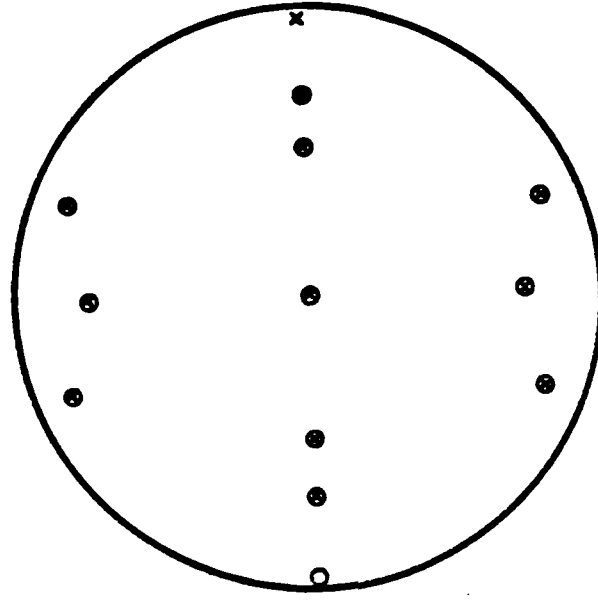


Scale mark 1cm

Figure 10: Typical morphology and crystal of TNT.



a) Untwinned crystal

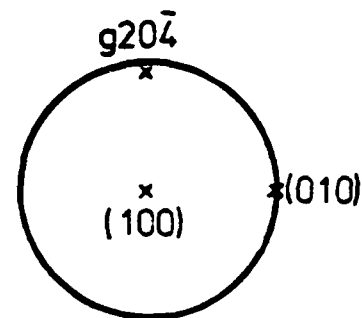


b) Twinned crystal

Figure 11: Stereographic representation of commonly observed crystal faces.



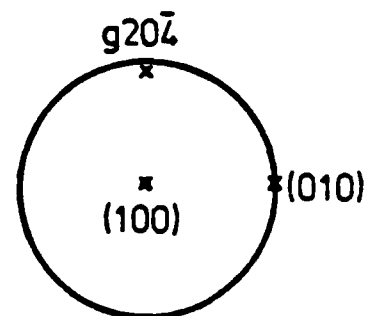
Figure 12: Topograph of a crystal grown from methanol.



Scale mark 1mm.

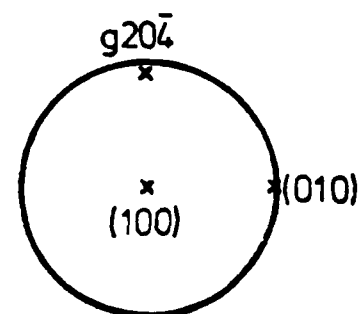
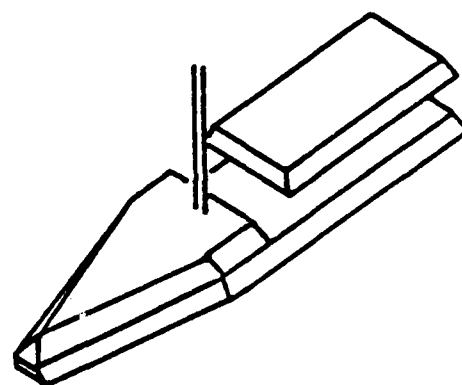


Figure 13: Topograph of a crystal grown from toluene.



Scale mark 1mm.

Figure 14: Topograph of a crystal grown from ethyl acetate.



Scale mark 1mm.

Figure 15: Topograph of a section from a crystal grown by slow cooling from ethyl acetate.