# IMPERFECTIONS IN TNT

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## THESIS

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Lieutenant, United States Navy

Submitted in partial fulfillment of
the requirements for the degree of

MASTER OF SCIENCE
IN
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# ABSTRACT

A literature search was conducted to determine the extent of explosive crystallographic data in the literature. The results of that search are reported herein. Explosives are extremely unstable and it is felt by the author that crystalline imperfections may play a major role in explosive mechanisms. A general discussion of crystal imperfections is presented and related to TNT. A study of TNT by conventional crystallographic means, x-ray diffraction and optical examination, is reported upon with results and recommendations for further study.

The writer wishes to express his appreciation for the assistance and encouragement given him by Professor John R. Clark of the U. S. Naval Postgraduate School in this investigation.

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## 1. Introduction.

The introduction of the X-ray diffraction technique and the electron microscope in the science of crystallography have resulted in spectacular advances in the crystallographer's knowledge of the microstructure of substances. Knowledge of crystal structure has aided the solid state physicist, the metallurgist and the chemist in predicting and analyzing the behavior of materials. Crystallographic data will be of importance to the explosives scientist in that the causes and the mechanisms of explosive sensitivity, brisance, and release of power are at the present imperfectly understood and crystallographic knowledge will aid in understanding these properties of explosives. Crystal structure as such will not directly correlate with explosive properties in that the crystalline forms of explosives are not basically different from non-explosive minerals. However, associated with any crystalline substances are certain imperfections of the crystalline state. Explosives by their nature are highly unstable substances. Any source of energy of sufficient magnitude can upset this delicate equilibrium. Crystalline impurities can be expected to magnify the essential chemical instability of the explosive. Imperfections which are non-destructive and commonplace in a non-explosive material may well be of sufficient magnitude in these unstable substances to cause or materially enhance the explosive capabilities of these compounds.

A literature search was conducted by the author to determine what crystallographic data were available. The results of that search are to be found in Table 1. The author entered the literature with more than fifty explosive compounds and discovered data on only twenty-two of these. It is obvious that the existent data on explosives is sketchy. Further information of a crystallographic nature is needed. The purpose of this work is

then to investigate imperfections in general and to lay groundwork for further more specific study of explosives and crystal imperfections.

TNT was selected as a readily available and satisfactorily well-behaved subject for an initial investigation. A possible TNT molecular arrangement appears in Fig. 1. Note that the model depicted is not the only possible arrangement as the nitro groups are capable of tilting from the depicted orientation. This yields right and left hand forms, i.e. enantiomorphism. This will be discussed at some length in the section on imperfections. Much of the crystallographic data available on TNT are sketchy and some even seemingly contradictory. The compound has been reported as a monoclinic structure, pseudo-orthorhombic, and orthorhombic. Investigations conducted by Burkardt and Bryden[1] indicate that as many as seven crystalline forms of TNT may actually exist. This may in part account for the multiplicity of data on TNT.

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[1] L. A. Burkardt and J. Bryden, X-Ray Studies of the Morphology of 2,4,6-Trinitrotoluene, NAVORD Report 2054, NOTS 748, 28 August 1953.

Fig. 1

## TABLE 1

| Explosive | Symmetry | Crystal Axes<br>$a_o$ | <br>$b_o$ | <br>$c_o$ |
|---|---|---|---|---|
| 2,4,6 Trinitrotoluene[2] | orthorhombic | 0.7586 | 1 | 0.5970 |
| Ammonium Picrate[2] | 2/m 2/m 2/m | 0.6799 | 1 | 1.0553 |
| PETN[2] | 4/m 2/m 2/m | 1 | | 0.506 |
| Picric Acid[2] | 2mm;$C_{2v}$ | 0.9691 | 1 | 1.0145 |
| Dinitroethane[2] | 4/m 2/m 2/m;$D_{4h}$ | 1 | | 0.8837 |
| 1,3,5-TNB[2] | 2/m 2/m 2/m;$D_{2h}$ | 0.9487 | 1 | 0.7252 |
| α -Lead Azide[3] | orthorhombic | 11.312 | 16.242 | 6.628 |
| β -Lead Azide[3] | orthorhombic | 17.508 | 8.844 | 5.190 |
| 3 -Lead Azide[3] | monoclinic | 17.60 | 8.83 | 5.10 |
| Lead Styphnate[3] | monoclinic | 10.02 | 12.54 | 8.00 |
| Lead Styphnate[4] (normal) | monoclinic | 10.06 | 12.58 | 8.05 |
| Lead Azide I[5] | orthorhombic | 11.41 | 16.31 | 6.66 |
| Lead Azide II[6] | monoclinic | 18.31 | 8.88 | 5.12 |
| 2,4 DNT[7] | orthorhombic | 6.11 | 23.11 | 5.17 |
| 2,6 DNT[7] | orthorhombic | 17.82 | 13.70 | 7.39 |
| 1,3,5 TNB[7] | orthorhombic | 12.8 | 27.0 | 9.8 |
| 2,4 DNT[7] | monoclinic | 15.83 | 15.27 | 8.15 |

[2] Porter and Spiller, The Barker Index of Crystals, Vol. 1, W. Heffer and Sons, Lt., 1951.

[3] Donnay and Nowacki, Crystal Data, The Geological Society of America, Memoir 60, 1954.

[4] Analytic Chemistry, Dec. 1955, 27:2014.

[5] Ibid, Nov. 1956, 28:1791.

[6] Ibid, Nov. 1956, 28:1792.

[7] R. W. Wyckoff, Crystal Structures, Interscience Publishers, Inc., 1951.

TABLE 1 (Continued)

| Explosive | Symmetry | Crystal Axes<br>$a_o$ | <br>$b_o$ | <br>$c_o$ |
|---|---|---|---|---|
| 1,3,6,8 Tetranitro-napthalene[7] | monoclinic | 26.3 | 7.77 | 5.55 |
| 2,4,6-TNT(low)[7] | monoclinic | 20.2 | 16.2 | 7.79 |
| 2,4,6-TNT(high)[7] | monoclinic | 21.35 | 6.05 | 14.96 |
| 2,4,6-TNT(3rd low form)[7] | orthorhombic | 20.07 | 6.09 | 15.03 |
| 2,4,6-TNT[8] | monoclinic | 21.35 | 6.05 | 14.96 |
| 2,4,6-TNT[8] | monoclinic | 79.60 | 6.09 | 14.99 |
| 2,4,6-TNT[8] | pseudo-orthorhombic | 159.20 | 6.11 | 15.03 |
| 2,4,6-TNT[8] | orthorhombic | 20.07 | 6.06 | 15.03 |
| Nitroguanidine[9] | orthorhombic | 17.58 | 24.84 | 3.58 |
| 1,8 Dinitronapthalene[10] | orthorhombic | 11.37 | 15.00 | 5.38 |
| 2,4,6-2', 4', 6' Hexa-nitrodiphenylamine[11] | orthorhombic | 11.75 | 19.10 | 7.43 |
| 2,4 Dinitrophenol[12] | orthorhombic | 6.11 | 23.11 | 5.17 |
| 4,6 Dinitro-rescorcinol[13] | monoclinic | 17.07 | 5.03 | 11.79 |
| 2,3,4,6-Tetranitro-aniline | Monoclinic | | | |
| 1,3,8-Trinitro-napthalene | monoclinic | | | |
| 1,5-Dinitronapthalene[16] | monoclinic | 7.85 | 16.26 | 3.70 |

[7] R. C. Wyckoff, Ibid

[8] L.A. Burkardt and J. Bryden, X-Ray Studies of the Morphology of 2,4,6-Trinitrotoluene, NAVORD Report 2054, NOTS 748, 28 August 1953.

[9] Analytic Chemistry, Jan. 1951, 23:205

[10] Ibid, Aug. 1951, 23:1188

[11] Ibid, Feb. 1952, 24:592

[12] Ibid, Nov. 1952, 24:1863

[13] Ibid, Dec. 1952, 24:2008

[14] Ibid, Nov. 1953, 25:1774

[15] Ibid, June 1954, 26:1096

[16] Ibid, Aug. 1954, 26:1390

## 2. A General Discussion of Crystalline Imperfections.

The perfect crystal per se is non-existent. As atomic and solid state physics progress further into the fundamental states of matter it becomes more certain that imperfection is the naturally occurring state of matter. As early as 1914, C. G. Darwin propounded the theory that naturally occurring crystals did not form in the precise perfect structures that were ascribed to them. His proposal was that the crystal structures were a mosaic pattern, Fig. 2a. He demonstrated mathematically that an x-ray beam would be trapped in a crystal of perfect lattice structure as in Fig. 2b. The beam would be reflected and re-reflected to the point of extinction or at the very best only an exceptionally weak beam would escape the crystal. The intensities of the diffracted beams are confirmation of the accuracy of Darwin's calculations.

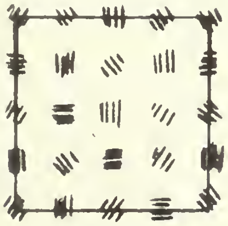

Fig. 2a

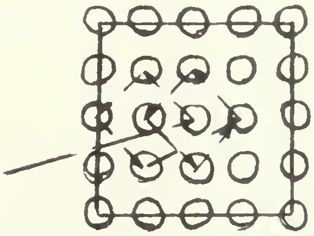

Fig. 2b

Imperfections take many and varied forms, a few of which will be discussed in the course of this study.

A. Steric Hinderance

Considering the TNT molecule as a function of bond radii[17] we note in Table 2[17] the bond radii of the constituent atoms of TNT.

The TNT molecule has been reported as a variety of crystal-structures. As an example of possible steric hinderance let us examine the Wyckoff

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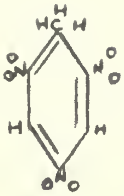
[17] F. H. Gedman and F. Daniels, Outlines of Physical Chemistry, 7th Ed., John Wiley and Sons, Inc., 1943.

TABLE 2

| Bond Structure | Radius (in Angstrom units) |
|---|---|
| Hydrogen | 0.03 |
| C(Benzene C-C) | 0.69 |
| C(Benzene C-H) | 0.77 |
| C(Single Bond) | 0.77 |
| N(Single Nitrate) | 0.70 |
| O(Single Bond) | 0.66 |

A calculation of the planar length of the TNT molecule reveals it to be 6.72 Å. This figure was obtained as follows:



| | |
|---|---|
| The H-C Bond (0.30 0.77) cos 54° | 0.63Å |
| The C-C Bond (0.69 0.77) | 1.46Å |
| Distance across benzene ring | 2.76Å |
| The C-N Bond (0.69 0.70) | 1.39Å |
| The N-O Bond (0.70 0.66) cos 54° | 0.80Å |
| The total planar TNT length is | 7.04Å |

The factor sin 108° arises from the fact that the non-planar bonding angle for both the C and N atoms is 108° and the projection yields consine of ½ the angle or cosine 54°. The distance across the benzene ring was determined by constructing similar triangles and summing the planar distances.

The planar width of the TNT molecule is found by the same technique to be

| | |
|---|---|
| The N-O Bond | 0.80Å |
| The N-C Bond | 1.39Å |
| Distance across the benzene ring | 2.76Å |
| The C-N-O Bonds | 2.19Å |
| The total planar width of TNT is | 7.14Å |

TNT (High) monoclinic form from Table 1. The structure as reported by Wyckoff is

| $a_o$ | $b_o$ | $c_o$ |
|---|---|---|
| 21.35 | 6.05 | 14.96 |

Figs. 3a and 3b show possible molecule arrangements within the simple monoclinic lattice. Fig. 3a depicts a non-hindered arrangement and Fig. 3b shows how steric hinderance could alter the primitive cell arrangement.

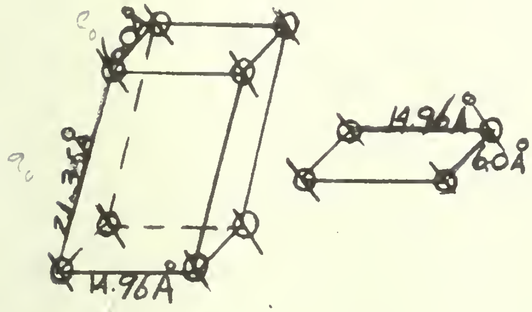


Fig. 3a

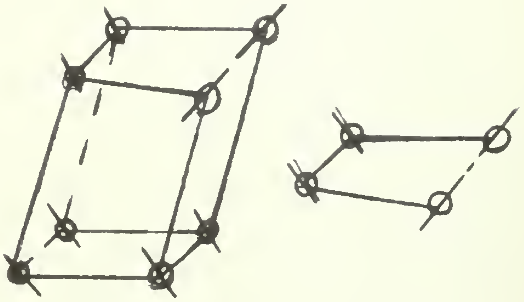


Fig. 3b

Should any two adjacent molecules on the $b_o$ axis become reoriented parallel to the $b_o$ axis they would overlap. This overlapping according to Pauli's exlusion principle is impossible and a subsequent deformation of the primitive crystal would result.

B. Interstitial and Substitutional Molecules.

The TNT used for crystal growth was obtained from the Eastman-Kodak Company and was presumed 95%-99% 2,4,6-TNT. The major impurities were TNB and traces of 2,4 and 2,6 DNT. These impurities can manifest themselves as substitutional molecules or interstitial molecules in the crystal lattice. Fig. 4a shows a substitutional impurity and Fig. 4b shows an interstitial impurity. Impurity atoms modify the energy of the crystal.

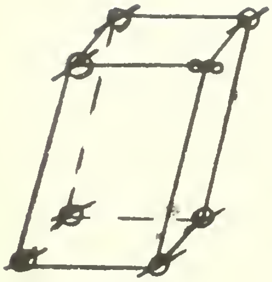


Fig. 4a

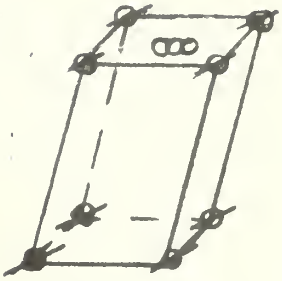


Fig. 4b

### C. The Enantiomorphic Structure of TNT.

As we noted in the introduction, TNT exhibits enantiomorphism, i.e. it possesses left and right hand forms due to the ability of the 2,6 nitro groups to rotate. This rotation or tilting of the nitro groups produces dissimilar TNT molecules although the chemical species remains unchanged. This is capable of altering the cell structure by destroying the repetitive pattern of the unit cell. A mirror image is produced across adjacent cell boundaries. Fig. 5a presents a possible primitive cell structure and Fig. 5b illustrates the increased cell dimensions made necessary to restore the symmetrical basic structure after an enantiomorphic repetition has occurred. Due to the complexity of the three dimensional problem presented in this imperfection a planar view has been presented.

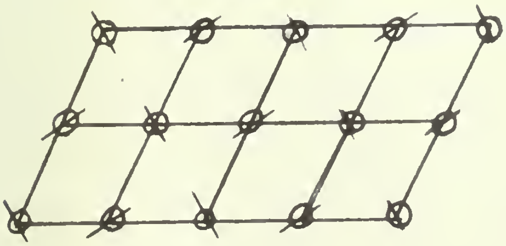


Fig. 5a

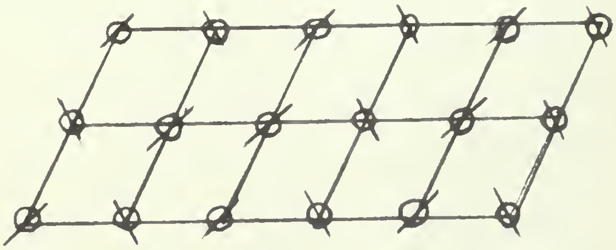


Fig. 5b

ø Right handed form of 2,4,6-TNT

⦸ Left handed form of 2,4,6-TNT

Note that a repetition of the ø-ø formation in the upper row has resulted in a complete pattern change for the crystal stacking and although a symmetrical pattern has been re-established in the lattice it is not a repetition of the original pattern. This non-symmetry of pattern leads to the formation of crystal twins, which will be discussed at some length in Section G.

D. Vacancies.

Vacancies may be defined as holes in a lattice structure. Vacancies are generated as equilibrium imperfections during crystal growth or by thermal vibrations in the lattice structure. Vacancies occur as two main types, Frenkel defects[18] and Shottkey defects. Frenkel defects are shown in Fig. 6a and Shottkey defects in Fig. 6b. Shottkey defects are more prevalent in ionic crystals than in molecular crystals and may be caused by imperfection complexes.

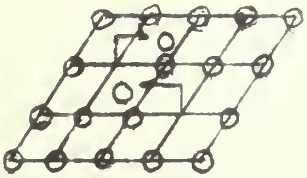


Fig. 6a

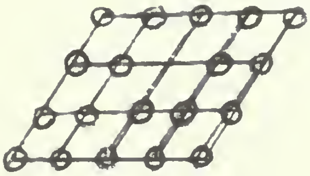


Fig. 6b

Note that Frenkel defects are produced by the displacement of a lattice molecule from its normal lattice position to an interstitial position, whereas the Shottkey defect is a complete abscence of a lattice molecule. Although motion in a molecule is more restricted than in an atom, vacancies are capable of uniting with one another to form very large holes in the crystal lattice. Conversely, vacancies are capable of combining with

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[18] Committee on Solids, Imperfections in Nearly Perfect Crystals, John Wiley and Sons Inc., 1952, p. 34.

interstitial atoms whereupon both imperfections are cancelled out of the crystal.

### E. Dislocations.

The dislocation is so successful in explaining crystal properties that it is probably the most overused explanation of crystalline properties. The simplest explanation of a dislocation is that it is a plane of vacancies or when viewed differently an added plane of interstitial atoms. The problem of dislocations is much more complex than this simple analogy would lead one to believe. Consequently only some of the simpler concepts will be presented. Fig. 7 shows a Taylor-Orowan[19] or edge dislocation.

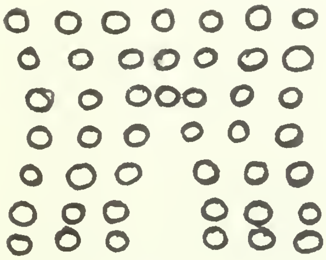

Fig. 7

Note the missing plane of atoms in the lower half of the figure. The lattice is under compression above the slip plane and under tension below it. Fig. 8 demonstrates the mobility of the dislocation and explains why the concept was first introduced as a method of explaining shear displacement in the plastic flow of crystals. The molecules in the lattice have moved to the right one lattice distance d. The edge dislocation depicted in Fig. 7 and Fig. 8 moves perpendicular to the slip plane.

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[19] Ibid, p. 45.

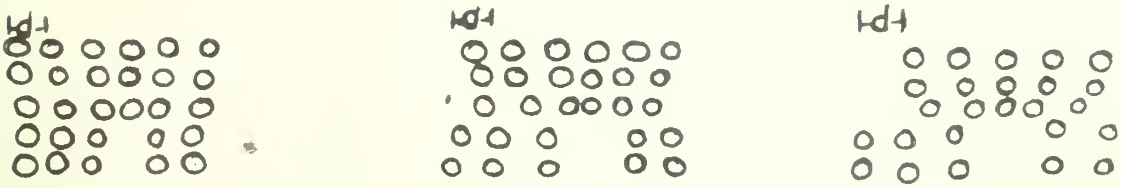

Fig. 8

Another type of dislocation is the Burger's or screw type dislocation. This type of dislocation has proved to be of great value in the theory of crystal growth. Frank[20] has suggested that a growing crystal is not perfect but contains dislocations. Fig. 9 shows a screw dislocation and illustrates the role it plays in the Frank theory of crystal growth.

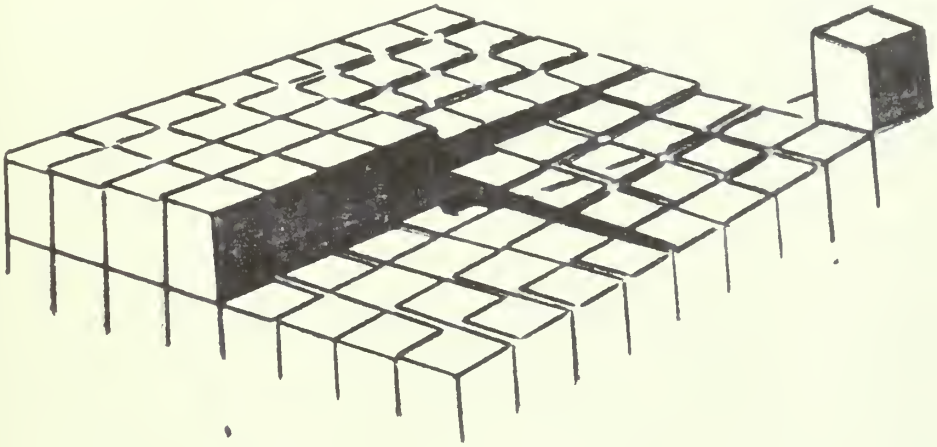

Fig. 9

A screw dislocation meets the surface at right angles and connects to the crystal surface by a step. Atoms are absorbed at the crystal surface and diffuse to the step. The atomic layer thus formed is never completed since the upper crystal surface is a spiral ramp. The crystal can

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[20] F. C. Frank, The Theory of Crystal Growth, Advances in Physics, Vol. 1 1952, p. 91.

thus grow indefinitely without a nucleation of new layers. As the crystal first forms with the end point of the dislocation fixed succeeding atoms tend to form a spiral around the point. The outer sections have further to go to complete one revolution so the inner sections complete more revolutions per unit time. As the spiral develops, the inner sections acquire a higher degree of curvature which increases the local vapor pressure until it becomes greater than the equilibrium vapor pressure. This condition slows down the rate of spiral growth and soon an equilibrium is reached where:

(rate of advance/distance from dislocation) = (revolutions/unit time)

Thus a steady state is reached wherein the whole spiral rotates uniformly about the dislocation.

There are many other growth steps recognized. All have valid assumptions behind them and merely relate other approaches to the complicated problem of crystal growth. One of these approaches will be discussed in Section G. on twinning.

### F. Atomic Imperfections.

At the present, atomic imperfections of the type to be discussed are not in general explored by the chemical world. However, twenty-five years ago solid state imperfections of the type just discussed were empirically noted but not investigated by the general crystallographer. So speculation concerning atomic level imperfections seem justified.

Close examination of the TNT molecule reveals that the methyl group and 2,6 nitro groups almost touch, see Fig. 1. The unstable nitro structures are in a state of continual electronic flux. If it should happen that any of the hydrogen atoms on the methyl group exhibit deuterium or tritium structure, opportunity is provided for a cross-linking structure which would alter crystal structure.

Conversely, if in any way, a hydrogen molecule were separated from its rightful position in the molecule, cross-linkage would become necessary to satisfy the electron requirements of the molecule.

G. A Discussion of Growth Twins.

Burkardt and Bryden[21] as does Ito[22] note evidences of imperfections in their x-ray patterns and advance the theory that these imperfections may be caused by twinning. It might at this point prove advantageous to examine some facets of the theory of twinning.

Cahn[23] states, "A twin may be defined as a polycrystalline edifice built up of two or more homogeneous portions of the same crystalline species in juxtaposition and oriented with respect to each other according to well-defined laws."

Perhaps a further investigation of some of the terms in the definition is in order. Homogeneous—The individual parts of a twin may be referred to a single crystal lattice and each atom is everywhere related in the same way to its nearest lattice point, i.e. each part of a twin is a single crystal. Juxtaposition—The parts are in such intimate contact with the common surface that they cohere. This coherence may be as strong or even stronger than the internal cohesion of a single crystal. The "well-defined laws" are not as self-evident as Friedel, Mallard and Bravais, the early investigators of twinning, thought them to be. Much controversy has raged over just what constitutes a twin law. No single law has been found nor is one likely to be found which satisfactorily explains the myriad of

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[21] L. A. Burkardt and J. Bryden, X-Ray Studies of the Morphology of 2,4,6-Trinitrotoluene, NAVORD Report 2054 NOTS 748, 28 Aug. 1953, p. 15.

[22] Ito, X-Ray Studies on Polymorphism, Maruzen Co. Let., 1950, p. 111.

[23] R. W. Cahn, Twinned Crystals, Advances in Physics, Vol. 3, 1954, p. 363.

twinning phenomena. One explanation has been advanced by M. J. Buerger[24] which, although offered primarily as an explanation of growth twins, sheds much light on the general concept of twinning. A stable crystal is the lowest free energy state of a particular configuration of atoms. Any other structure results in an increase of free energy. A twin, being a combination of crystals, is obviously not in the lowest free energy state. Therefore, concerning outselves at the present with only the phenomenon of growth, let us postulate an explanation for the growth of a non-stable crystal. Every crystal contains a total of energy that sums up to the total contributed by the individual atoms in the crystal. Each atom has a series of coordination spheres which decrease rapidly with distance. The first coordination sphere of an atom, i.e. the one containing its nearest neighbors, is the heaviest contributor to the total energy associated with that atom. The next coordination sphere modifies this energy, as do each of its successive spheres, but each to a lesser extent than the preceeding. It appears that an atom can take part in a twin boundary layer if its primary coordination requirements are met. In examination of twins it is apparent that there is present a multiple structure, i.e. the primary crystal and an altered series of coordination structures which give rise to the twin boundaries. Buerger[25] states, "If the structure is of such a nature that, in detail, it permits a continuation of itself in alternative twin junction configuration without involving violation of the immediate coordination requirements of its atoms, the junction has low energy and the twin is energetically possible."

Let us now observe the growth of a twin structure. As the structure grows the first atom can locate anywhere. The second atom that arrives

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[24] M. J. Buerger, The Genesis of Twinned Crystals, The American Mineralogist, Vol. 30, July-August 1945, p. 469.

[25] _Ibid_, p. 472

on the scene must locate in such a way as to coordinate with the first to achieve its lowest possible energy level. The succeeding arrivals must coordinate with those already on the scene. At near equilibrium conditions a second layer of atoms is started only after the first layer is completed. It is possible for an atom to arrive at a non-equilibrium position. However, its fugacity $F_i^{'}$ $RT$ $\ln f_i$ $B_i(T)$ would be comparatively high and it would tend to lose its position due to atomic bombardment or thermal agitation. However, if the growth medium is saturated or supersaturated, it is possible for nuclei to form in several places at once. If a small group of atoms arrive at the crystal lattice at the same time their mutual coordination level may be sufficiently low for them to remain in position and a twinned lattice is begun. With the aid of Fig. 10[26] let us analyze the French school of twin formation and modify it with Buerger's restrictions. The crystal plane PP is being covered by a layer

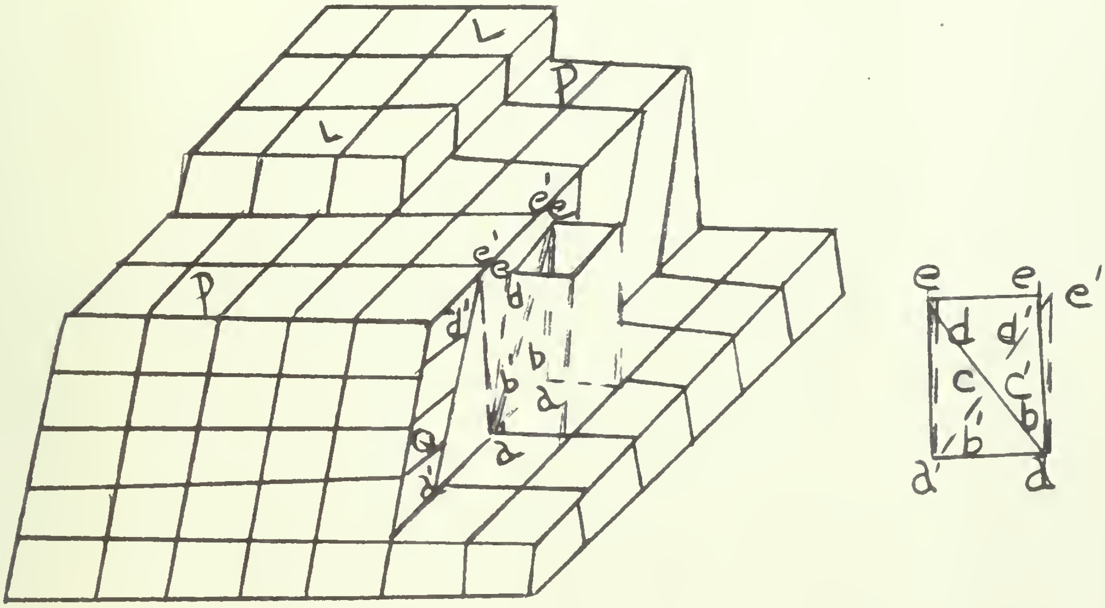

Fig. 10

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[26] Ibid, p. 474.

of crystals LL. The cliff QQ may be formed at any time during cell growth if very rapid growth has occurred. Now although the cliff is maintained for only milliseconds, it provides a place of multiple attachment for a preformed cluster of cells, i.e. the foot and side of the cliff offer a reentry face of greater geometric attachment than a normal single layer and atom-by-atom* deposit would offer. Therefore, according to the French theory, the twinned pattern is initiated solely because of subminimal energy requirements and geometric considerations. The vast crystal itself acts as an energy buffer to the dislodgement of the smaller unit due to bombardment by other atoms or from thermal vibrations. The small cluster abcde arrives at the crystal and being elastic superimposes itself on the crystal points a'b'c'd'e' in such a manner that aa'bb'cc'dd'ee' are coincident. The angle of obliquity is then 1/2 the solid angle $e'ae_1$. It is here that Buerger amends the French theory. He postulates that the geometric lattice figure provides necessary but not sufficient conditions for twinning. The sufficiency is supplied by requiring low energy junctions from twinned to untwinned structure. This implies a continuous structure in the nearer coordination zones of the twinned junction. This stipulates a partial lattice fit in planes other than the twinning plane. In most observed twinned crystals this is the actual situation.

## 3. Experimental Procedure.

### A. Introduction.

The methods of conventional crystallography were utilized in the study of TNT crystals. X-ray diffraction patterns and optical properties of the crystals were investigated. The x-ray diffraction techniques used were the Laue' pattern, the rotating crystal pattern, and the precession patterns. Each of the preceeding will be discussed in Section C.

### B. Growth of Crystals.

The method of crystal growth was a sublimation described by Burkardt amd Bryden[27]. The method was chosen because it required reasonably little care and provided a controlled atmosphere for the crystal growth. In essence the method is a sublimation under vacuum of any solid at any desired condensation temperature. In particular and as actually performed by the author in the course of the thesis work, it is a sublimation and condensation at 78°C. The apparatus is sketched in Fig. 11.

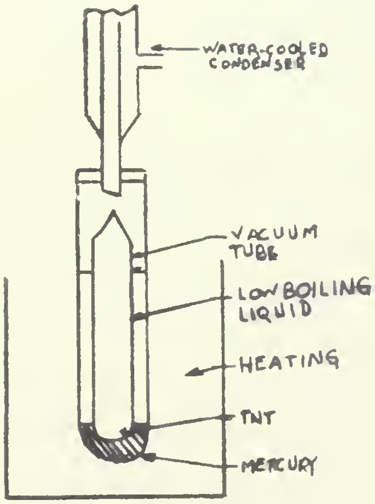

Fig. 11

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[27] L. A. Burkardt and J. Bryden, X-ray Studies of the Morphology of 2,4,6-Trinitrotoluene, NAVORD Report 2054, NOTS 748, 28 Aug. 53, p. 3.

The TNT, Eastman Kodak, 95-99% pure 2,4,6-TNT, is placed in a tube which is then evacuated and sealed. The evacuated tube is placed in a larger tube and mercury is *added to a sufficient depth to cover the entire sample*. Ethyl alcohol is added on top of the mercury and the outer tube is fitted into a reflux condenser. The apparatus is then put into a constant temperature water bath which is held at 83°C ± 2°. The principle is to have the heating bath at a temperature just above the melting point of TNT, 80°C. The condensing liquid is below the melting point providing a temperature differential. The mercury heats to the temperature of the water bath melting the TNT. As the ethyl alcohol refluxes it provides a constant temperature surface, 78°C, for condensation and recrystallization of the sublimated TNT vapors.

The crystals resulting from this method are very thin needles, which vary from colorless to an extremely light straw color. Their size has been smaller than is desirable for ease of x-ray analysis. However, analysis has been made of the growth method and the author believes consistently satisfactory crystals can be obtained if the following causions are observed.

1. *Extreme* care must be exercised to insure that no TNT particles adhere to the sides of the evacuated tube as these provide an excessive source of nucleation points which results in a large number of tiny crystals.

   To overcome this effect, excess mercury should be added to more than merely cover the sample area.

2. As small a temperature difference as is feasible should be maintained, i.e. as near 81°C as it is possible to maintain the

heating bath. This controls the rate of sublimation and cuts down the possible nucleation points, resulting in fewer but larger crystals.

3. During evacuation but prior to sealing the vacuum tube, neck it down, to provide a partial bottleneck condensation surface. This will have the effect of concentrating the bombardment of sublimed particles at a point source of condensation. It is felt that this concentrates the particles onto nuclei which are already formed rather than allowing the formation of more nuclei.

It should not be construed from the foregoing that large crystals were not obtained. Many satisfactory crystals were obtained. However, the crystals exhibit an unusually high surface tension. Upon separation from the glass tube the larger exhibited a distressing tendency to shatter. This may be partially avoided by coating the inner tube with silicone mold release of the type used to coat plastic molds.

The problem therefore is not one in growing large crystals but rather growing them in such numbers to offset the mortality of separation from the glass tube and accidents in mounting.

C. X-ray Diffraction.

The major effort in the crystal analysis has been an x-ray examination of the TNT crystals grown by the method of 3B. An optical goniometer was unavailable and the crystals were aligned by x-ray photography. Laue' patterns were taken in an effort to establish a crystal plane. A specimen pattern is shown in Fig. 12. Note the line of spots bisecting the picture. This is an equator line and the linear bisecting of the pattern indicates a bi-fold symmetry with the crystal aligned roughly to a crystalline face.

Fig. 12

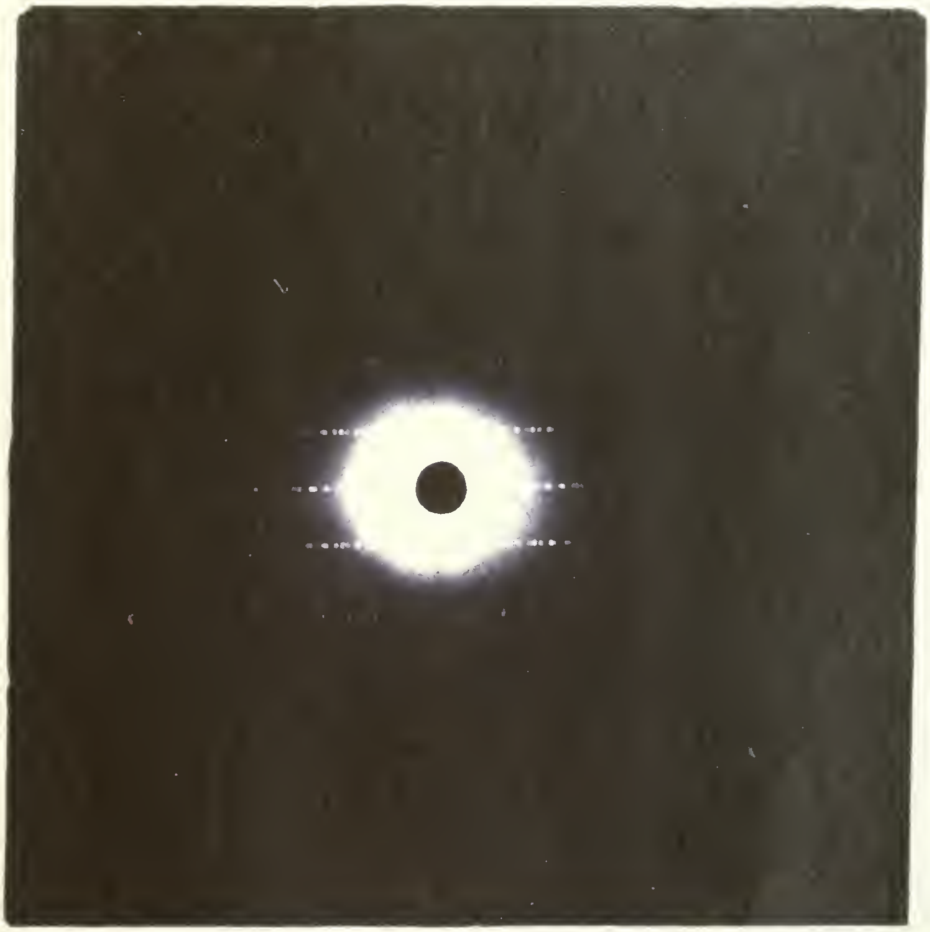
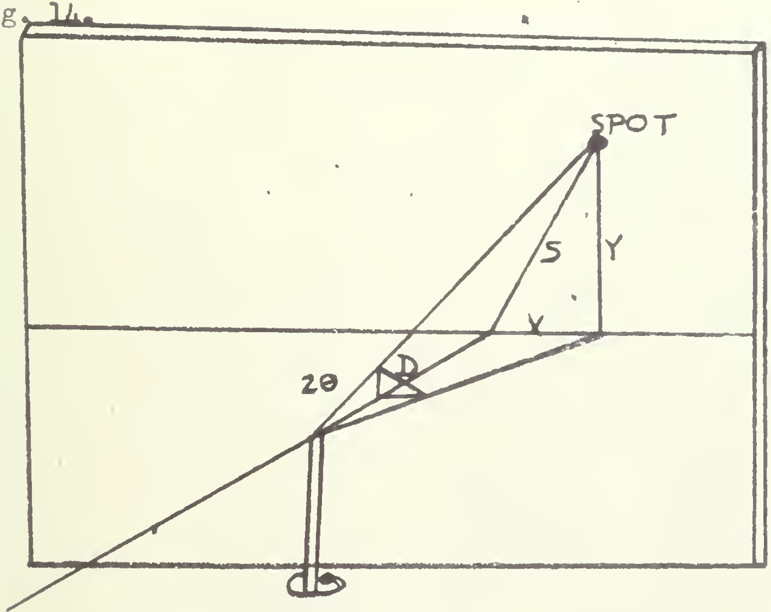


Fig. 13

Laue' patterns indicate planar symmetry and can, by analysis of the shape and general size of the spot with reference to other spots on the same photograph, indicate lattice alignment. The spots on the film exhibit various degrees of elipticity as the lattice atoms are diffracted by the x-ray beam. The angle at which the beam intersects the crystal atoms determines the elipticity of the diffracted spot. In general lattice parameters are not derived from Laue' patterns, which leads to the next step in the analysis, the rotating crystal method. Fig. 13 illustrates a rotating crystal photograph of TNT under chromium radiation. The rotating crystal photograph in addition to refining the alignment of a pattern yields interlattice distance measurements by the method illustrated in Fig. 14.



(1) $d = \frac{N\lambda}{2\sin\theta}$

(2) $\tan 2\theta = \frac{S}{D}$

substitute (2) into (1)

(3) $d = \frac{N\lambda}{2\sin\left(\frac{1}{2}\tan^{-1}\frac{S}{D}\right)}$

IN TERMS OF FILM COORDINATES

(4) $d = \frac{N\lambda}{2\sin\left(\frac{1}{2}\tan^{-1}\frac{\sqrt{X^2+Y^2}}{D}\right)}$

The culmination of the alignment is photographing the crystal with the Buerger precession camera. The precession camera photographs the reciprocal lattice of the crystal with no distortion. The initial purpose of the precession photographs was to determine the general shape of the clouds at the reciprocal lattice points. Now however, the author feels that a complete structural determination of the TNT is in order.

This may prove to be very difficult due to the complications introduced by crystal imperfections.

Investigation of gross crystalline imperfections under polarized light was hampered by inadequate refractive index liquids. However, the liquids at hand and a petrographic microscope gave no evidence of gross imperfections such as twinning or surface strain. Investigation of the TNT as received from Eastman, unpurified nitroguanidine, TNB, and RDX all revealed definite fringe patterns indicating surface strain, twinning on a gross scale, or perhaps both of these phenomena.

## 4. Results and Conclusions.

Figs. 15 and 16 show Buerger photographs. Fig. 15 is a zero layer pattern taken in unfiltered molybdenum radiation. Note the heavy radial streaking. Fig. 16 is the same pattern as above using zirconium filter. Most of the radial streaking has been eliminated from which it may be concluded that the streaking was due largely to white radiation. A two-fold symmetry will be noted in the reciprocal lattice pattern. However, due to uncertainty as to the crystal axis around which the symmetry occurs and a lamentable lack of time for further photography no definite conclusions as regards structure can be made at this time. The two-fold symmetry could be either monoclinic or orthorhombic. The residual streaking in Fig. 16 may be due to either inadequate monochromation of the x-ray beam or due to impurities in the crystal. If it is due to the impurities present some definite conclusions can be drawn as regards the nature of these impurities. As has been indicated in the previous section, the optical examination of these crystals revealed no gross imperfections such as twinning, or surface strain. Therefore the majority of the imperfections present in this species of TNT crystal must of necessity be of the submicroscopic type such as vacancies, interstitial and substitutional impurities and possibly submicroscopic twin areas.

Measurements on the rotating crystal pattern in Fig. 13 yielded a cell distance of 6.10 Å. This is in agreement with the $b_o$ axis reported by Burkardt and Bryden[28] for the high temperature monoclinic form of TNT. Although one measurement is an incomplete analysis it indicates a partial confirmation of Burkardt and Bryden's findings.

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[28] L. A. Burkardt and J. Bryden, X-Ray Studies of the Morphology of 2,4,6-Trinitrotoluene, NAVORD Report 2054, NOTS 748, 28 August 1953, p. 5.

Fig. 15

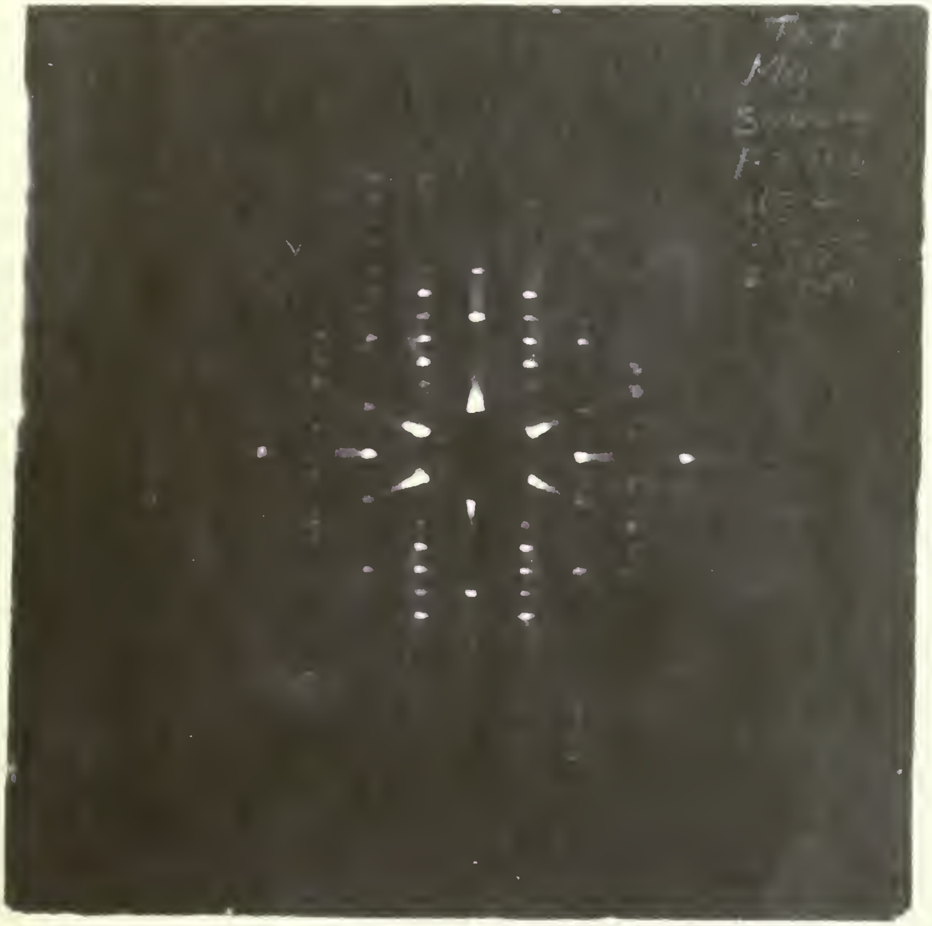

Fig. 16

## 5. Recommendations For Further Study.

When satisfactory refractive index liquids are received, it is recommended that a refractive index study be conducted on the sublimed TNT crystals.

More precession patterns are recommended in an effort to definitely establish the structure of these sublimed crystals.

It is also recommended that attention be directed to perfecting the crystal growing techniques. Some crystals required one week exposures to produce clear patterns. Consistently larger crystals are a must in future work.

Investigation of the precession camera method of crystal alignment is recommended as it may prove a more satisfactory method than the Laue' pattern method.

# BIBLIOGRAPHY

1. R. C. Evans, An Introduction to Crystal Chemistry, Cambridge University Press, 1939.

2. A. H. Cottrell, Dislocations and Plastic Flow in Crystals, Oxford at the Clarendon Press, 1953.

3. W. H. Bragg and W. L. Bragg, The Crystalline State, G. Bell and Sons, Ldg., 1955.

4. F. C. Phillips, An Introduction to Crystallography, Longmans, Green and Co., 1946.

5. M. J. Buerger, Elementary Crystallography, John Wiley and Sons, 1956.

6. Dislocations and Mechanical Properties of Crystals, John Wiley and Sons, 1957.

7. R. W. Cahn, Twinned Crystals, Advances in Physics, Vol. 3, pp. 363-446, 1954.

8. F. Seitz, Imperfections in Nearly Perfect Crystals, John Wiley and Sons, Inc., 1952.

9. M. J. Buerger, The Genesis of Twin Crystals, The American Mineralogist, Vol. 30, July - August 1945.

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