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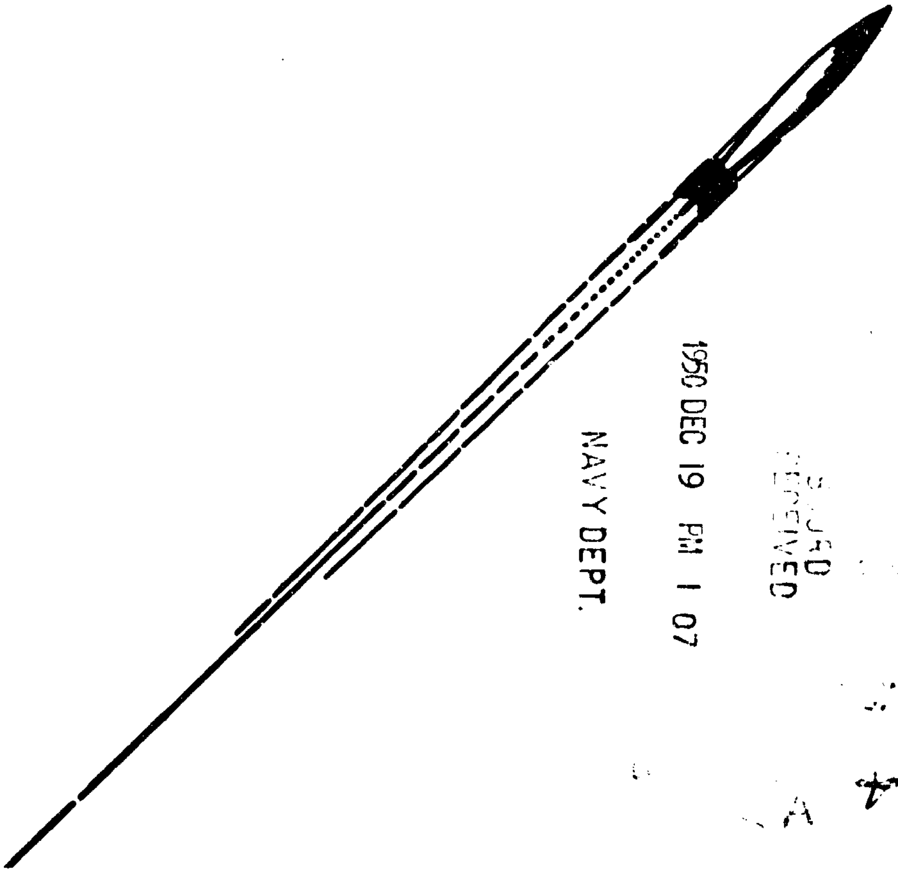
NAVORD REPORT 1252

# THERMAL EXPANSION STUDIES ON TNT



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*Commander*

L. T. E. THOMPSON, PH.D.
*Technical Director*

# THERMAL EXPANSION STUDIES ON TNT

By

**Wm. Roderick Eubank**

and

**Robert W. Van Dolah**

*Research Department*

NAVORD REPORT 1252
NOTS 316

China Lake, California
24 August 1950

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## ACKNOWLEDGMENT

The author acknowledges the work of E. R. Dalbey of the Organic Chemistry Branch in purifying the TNT used in this investigation. In addition, appreciation is expressed to G. B. Shook of the Applied Science Division for obtaining heating curves for TNT, employing apparatus for the determination of specific heats, and to H. J. Gryting of the Process Development Branch for making a purity estimation on the TNT used.

## FOREWORD

The investigation described in this report is a part of a comprehensive program to add to the fundamental knowledge of the important military explosive, alpha-trinitrotoluene (TNT). Many such studies have been neglected because of lack of interest in times of peace and the urgency of production and utilization problems in times of war. The problem of determining thermal expansion of TNT was suggested by the sensitivity to small temperature changes resulting in unpredictable fracture of large crystals grown either from solution or the melt. This work is incomplete awaiting, as it must, further elucidation of the crystallography of TNT for complete explanation of the phenomena observed.

This study was begun under Task Assignment NOTS-37-Re2c-19-2 and completed under an allocation from Technical Overhead funds, Local Project 586.

This report has been reviewed for technical competence by W. M. Cady, A. L. Olsen, and L. A. Burkardt.

J. H. SHENK
*Head, Research Department*

Released by:

L. T. E. THOMPSON
*Technical Director*

## ABSTRACT

Coefficients of thermal expansion for the three crystallographic axes of alpha-TNT have been determined. The coefficient for the intermediate and long axes is about 50 × $10^{-6}$ in./in./°C, and that for the short axis averages about four times this value. The thermal expansion along the short axis showed marked changes at temperatures from 55° to 65°C. Plastic flow was observed along the intermediate and long axes at temperatures 8° or 9°C below the melting point. Little or no flow was noted along the short axis. These observations indicate that TNT crystals have anisotropic physical properties. Thermal-shock experiments showed that fracture occurs along the short axis perpendicular to the long axis. Heating curve data did not uncover an energy change for TNT below the melting point.

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## INTRODUCTION

Alpha (2,4,6-) trinitrotoluene employed separately or as a major component of numerous explosive compositions is one of the most important and widely used of the high explosives. Although thousands of tons of this compound have been produced and many refinements made for its manufacture and utilization, certain basic physical properties are not known. For example, the changes in such properties as heat conductivity, specific heat, expansion, elastic properties, solubility of gases, and rate of solid phase reaction with changes in temperature have been studied insufficiently or not at all. It is difficult, therefore, to explain and cure certain deleterious properties observed for this valuable material, such as poor mechanical strength, change in physical characteristics during storage, formation of nonuniform castings, and abnormal grain growth.

One of the most important of the unknown basic properties is thermal expansion. A knowledge of this property will very likely permit a better understanding of some of the difficulties in manufacturing and storing warheads containing TNT. The only published work on the thermal expansion of TNT is that of the Russian investigator Mantrov (Ref. 1), who determined only volume expansion for a limited temperature range. The method employed was a modified Dulong and Petit procedure, and the quantitative compositions of the explosive mixtures were not given. These data have not yet appeared in either the *International Critical Tables* or the *Landolt-Bornstein Physikalisch-Chemische Tabellen*.

In the present study the coefficients of thermal expansion along each of the crystallographic axes were determined. Several methods were considered before a satisfactory one was accepted. A dilatometric method was abandoned because of the necessity of using large crystals and the difficulty of obtaining these. The sensitivity of large crystals of TNT to temperature changes is another deterrent to this method. The interferometer for thermal expansion employs small specimens but is difficult to operate and calibrate. Therefore, it was decided to try a method employing one of the recently developed transducers, which are relatively easy to use and calibrate.

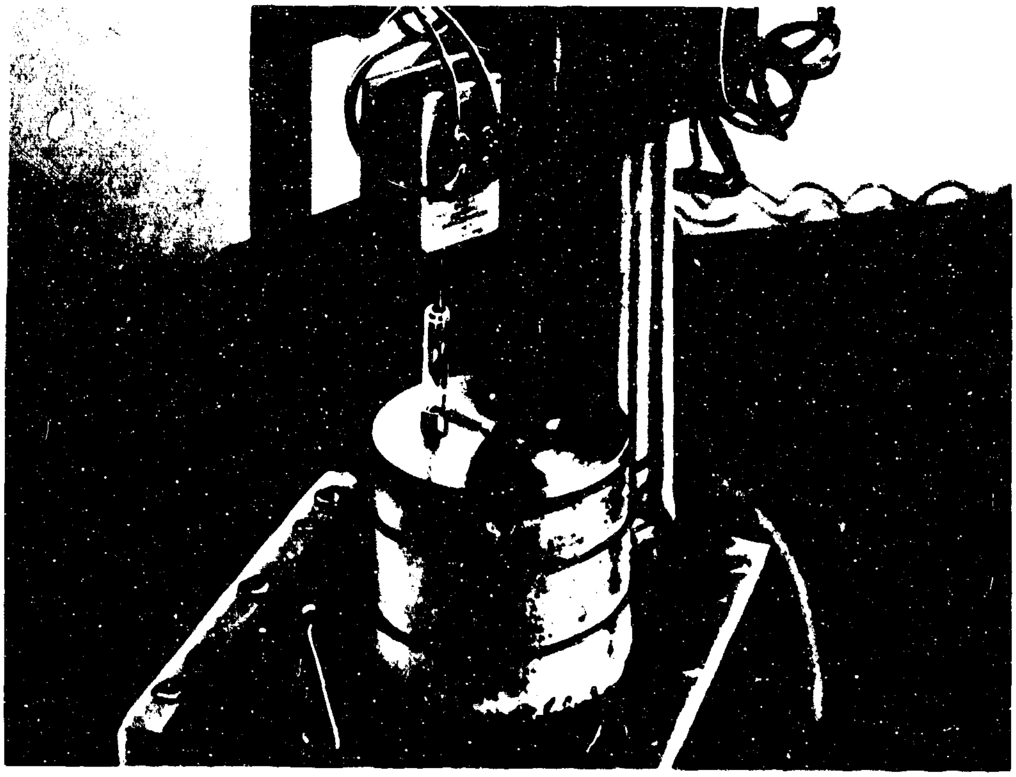

Fig. 1. Apparatus Employed in Expansion Measurements Including Statham Gage, Fused Silica Connecting Rod, and Nichrome-Wound, Oil-Filled Vycor Heating Vessel.

## EXPERIMENTAL PROCEDURE

### *APPARATUS*

The apparatus designed for the determination of thermal expansion along the three crystallographic axes of TNT makes use of a suitable transducer (Statham gage, Ref. 2) and a sensitive galvanometer. The apparatus used in these tests, including the Statham gage, fused quartz connecting rod, heating vessel, and supporting stand, is shown in Fig. 1. By employing a simple circuit of variable resistances and utilizing materials of known expansion, displacement in the system was calibrated in terms of galvanometer deflection. The displacement transducer element consists of a frame supporting a movable armature by means of two thin cantilever plates. Four sets of constantan filaments are strung under initial tension between the frame and armature in such a manner

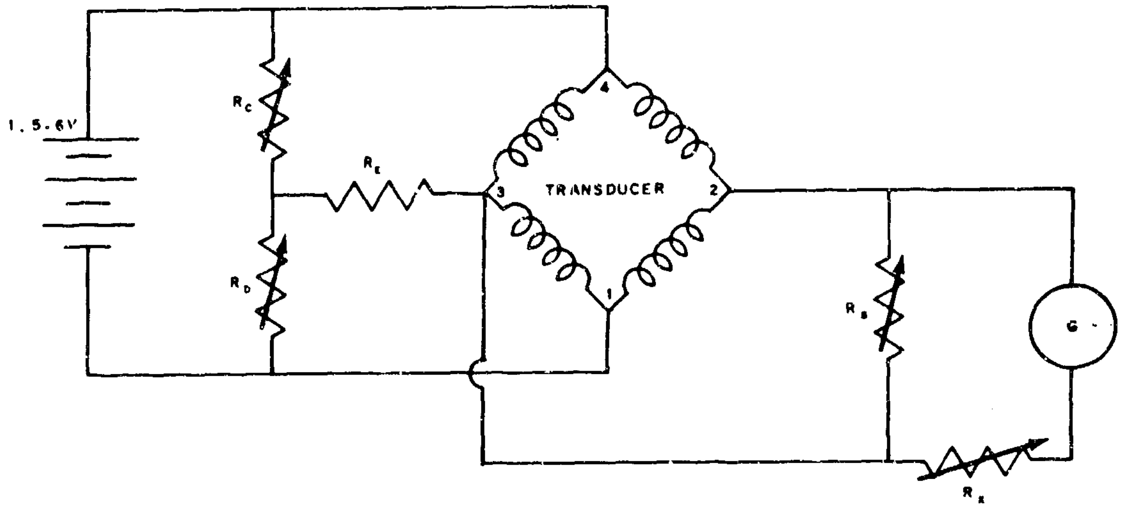

Fig. 2. Transducer Circuit for Measuring Displacement. $R_C$, $R_D$, $R_S$, and $R_X$ are decade resistance boxes with a range of 0 to 100,000 ohms; $R_E$ is a fixed wire-bound resistor with a resistance of 5,000 ohms; and $G$ is a suspension galvanometer with a sensitivity of 0.0013 μamp/mm.

that when the armature is displaced longitudinally, two of the sets of filaments are elongated, while the other two sets are shortened. The elongated filaments increase in resistance, while the resistance of the shortened filaments decreases. The change in resistance of the filaments is proportional to their change in length. The transducer is so wired that the filaments are connected in a Wheatstone bridge circuit, as shown in Fig. 2. The resistance change of the filaments alters the electrical balance of the bridge so that an electric current is caused to flow in the galvanometer circuit. The galvanometer deflection indicates and is proportional to the displacement.

The heating chamber was a 250-ml Vycor beaker with the flange cut off. An aluminum top with holes for a thermometer, stirrer, and connector to the gage was mounted on the Vycor vessel. The outside of the vessel was wound with resistance wire, then covered with asbestos paper. Connections were made to a variable transformer in order that various rates of heating could be achieved. This vessel was filled with an oil (SAE 10) in which TNT was insoluble. The oil was stirred by means of a variable-speed stirrer. The heating chamber was held in a supporting vise mounted on a heavy instrument stand to minimize the effect of vibrations. The transducer was rigidly attached to the top of the stand and could be raised or lowered in place by means of a rack gear.

A circuit diagram for the expansion measuring apparatus is given in Fig. 2. Resistances and other circuit components are listed. Variable resistances were employed in order that the sensitivity of the galvanometer could be varied and the bridge balanced for various pressures on the gage. Once optimum sensitivity of the galvanometer was established, however, it was held constant for all measurements. The battery voltage and the speed of the stirrer were also essentially constant from experiment to experiment.

For each determination, the galvanometer deflection was read at given temperature intervals, usually of 1°C. The resistances $R_S$ and $R_X$ (Fig. 2) were 12 and 1,000 ohms, respectively. The resistances $R_C$ and $R_D$ were varied from about 10,000 to 20,000 ohms, on the average, to bring the galvanometer to zero for each mounting.

### *CALIBRATIONS*

An effort was made to hold the expansion of the apparatus to a minimum. The heating vessel (Vycor, expansion coefficient, $0.8 \times 10^{-6}$ in./in./°C) and the connecting rod (fused quartz, expansion coefficient, $0.5 \times 10^{-6}$ in./in./°C) obviously have very low expansions. Nevertheless, it was considered advisable to determine and correct for the small expansion inherent in the apparatus. Three determinations (Table 1) were made, therefore, with no specimen in place; that is, with the fused quartz connecting rod resting on the bottom of the Vycor vessel. The result of these experiments indicates that a small average correction for expansion of the apparatus of 0.060 cm deflection per °C was required. This correction, consequently, was applied in calibrating displacement in terms of galvanometer deflection with materials of known expansion.

The materials of known expansion employed were Pyrex glass with an expansion coefficient of $3.2 \times 10^{-6}$ in./in./°C from room temperature to 200°C (Ref. 3); electrolytic copper with an expansion coefficient of $16.98 \times 10^{-6}$ at 50°C (Ref. 4), which is about the mid-point of the temperature range employed; and C.P. tin with an expansion coefficient of $22.69 \times 10^{-6}$ at 50°C (Ref. 4).

Both Pyrex glass and copper are isotropic. Tin belongs to the tetragonal crystal system but appears to contain random crystal orientations and hence uniform expansion in the temperature range employed (25° to 75°C). Calibration data for these three materials are presented in Table 2. It may be noted that the correction, $C$, for the expansion of the apparatus, previously determined (Table 1), is taken into account in column 6 and a value for net galvanometer deflection

## TABLE 1

Correction for Expansion of Apparatus at a Temperature Interval of 50°C

| Test Number | Galvanometer Deflection (cm) | Correction $C$ (cm/°C) |
|---|---|---|
| 1 | 2.95 | 0.059 |
| 2 | 3.15 | .063 |
| 3 | 2.90 | .058 |
| *Average* | -- | 0.060 |

## TABLE 2

Calibration of Galvanometer Deflection Using Materials of Known Expansion

| Material | Expansion Coefficient $E$ ($\times 10^6$) | Length $l$ (in.) | Temperature Interval $\Delta t$ (°C) | Galvanometer Deflection $D$ (cm) | Net Galvanometer Deflection $D-C\Delta t$ (cm) | Calibration $K$ (in./cm of defln. $\times 10^5$) |
|---|---|---|---|---|---|---|
| (1) | (2) | (3) | (4) | (5) | (6) | (7) |
| Pyrex glass | | | | | | |
| (1) | | | 54 | 9.05 | 7.45[a] | 4.64 |
| (2) | 3.2 to | 2.00 | 50 | 8.3 | 6.8[a] | 4.70 |
| (3) | 230°C (3) | | 50 | 9.2 | 7.7[a] | 4.16 |
| *Average* | | | | | | 4.50 |
| Electrolytic copper | | | | | | |
| (1) | | | 46 | 21.1 | 18.3 | 4.32 |
| (2) | 16.98[b] at | 1.014 | 50 | 23.7 | 20.7 | 4.16 |
| (3) | 50°C (4) | | 50 | 20.6 | 17.6 | 4.88 |
| *Average* | | | | | | 4.45 |
| C.P. tin | | | | | | |
| (1) | 22.69[b] at | 0.963 | 44 | 24.3 | 21.7 | 4.43 |
| (2) | 50°C (4) | | 50 | 28.6 | 25.6 | 4.27 |
| *Average* | | | | | | 4.35 |
| *Grand average* | | | | | | 4.43 |

[a] Because of the longer length of the Pyrex rod (2.00 in.) the fused silica connecting rod did not extend as far into the bath and only one-half of the correction factor ($C$) was employed.

[b] Over the temperature range employed (25° to 75°C) the two metals follow very closely the following expansion formula (Ref. 4): $l_t = l_0(1 + \alpha_t + \beta_t^2)$, where $\alpha \times 10^4$ is equal to 0.1596 and 0.2094 for copper and tin, respectively, and $\beta \times 10^7$ is 0.102 and 0.175.

calculated. The calibration constant, $K$, (see sample calculation, page 14) in inches displacement per centimeter of galvanometer deflection is tabulated in column 7, the average of all determinations being $4.43 \times 10^{-5}$ in./cm. The maximum deviation from this average is about 10 percent, but the average deviation is only 5 percent, which compares favorably with most expansion measurements on small-sized specimens.

The thermometer employed was checked by means of a chromel-alumel thermocouple, the junction of which was inserted into the oil bath near the sample. No appreciable difference, with the exception of response time, was observed.

## *PREPARATION OF MATERIALS*

A technical grade of TNT was carefully purified by dissolving in acetone, quenching in water, treating with sodium sulfite, washing with water, dissolving in carbon tetrachloride, again washing with water, dissolving in hot ethyl alcohol and allowing to crystallize.[1] The resulting fine white crystals were stored in the dark. Suitable crystals for expansion measurements were grown by dissolving this purified material in benzene, adding a seed crystal, and stirring in a constant-temperature bath at 30°C. Very slow evaporation of the benzene allowed production of pale yellow, transparent, well-formed crystals about 2 by 1 by 1/2 in. in size in a period of about 2 weeks. The purity of these crystals was estimated by using the set point method. The set point was 80.66°C, which yields a value of 99.68 mol percent purity when the Vant Hoff equation is used and an ideal solution is assumed. This assumes an ultimate set point of 80.90°C for pure alpha-TNT, which has not been definitely established.

These crystals were cut with a jewelers' saw to the approximate desired dimensions along each crystallographic axis and reduced further by grinding on fine emery paper. The broad, well-defined (010) face was used as a reference. The length of each specimen was measured to within 0.001 in. with a micrometer caliper before and after each expansion measurement.

The specimens to be investigated were mounted on the bottom of the heating chamber and kept upright and away from the walls of the vessel by means of coiled supports of copper wire. One of these supported specimens is shown beside the heater in Fig. 1.

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[1] This process will be discussed in a report to be prepared by W. A. Gey, E. H. Dalbey, A. F. Teague, and R. W. Van Dolah and released by NOTS.

## RESULTS

*DATA*

The data obtained for seven different crystals from one batch of purified TNT, on some of which duplicate determinations were made, are given in Table 3. Detailed data in the form of both heating and cooling curves are presented in Fig. 3, 4, 5 and 6 in which displacement is plotted against temperature for typical determinations for each of the crystallographic orientations. The rate of temperature change varied from 0.5° to 0.2°C per minute, with the lower rate being used near possible transition points.

Sample calculations are given for both the calibration constant, *K*, and the coefficient of thermal expansion, *E*, in the following section.

It may be noted (Table 3) that the expansion coefficients for TNT are relatively high and show a great difference between that for the short axis[2] and those for the other two axes. For example, the average values determined for the intermediate and long axes are 50.2 and 47.2 $\times 10^{-6}$ in./in./°C, respectively, as compared to an average value about four times as great, or 181 $\times 10^{-6}$ for the short axis. Thus it is seen that for the intermediate and long axes, expansions about four times that for mild steel (the usual warhead casing material) are obtained; whereas the short axis shows expansions about 15 times as great. For comparison, the expansion coefficient of hard rubber is about 80 $\times 10^{-6}$.

From Fig. 3 and 4 it is evident that the expansion along the short axis of TNT is not constant between room temperature and its melting point. In Fig. 3, at 64°C, an abrupt change in slope in both the heating and cooling curves occurs at points B and D, respectively. From room temperature to about 64°C the average of the heating and cooling curve determinations for thermal expansion is 159 $\times 10^{-6}$. From 64° to 79.5°C this average value increases by about 70 percent to 270 $\times 10^{-6}$. Another less pronounced inflection point may be seen to occur in the neighborhood of 55°C. Such inflection points have been noted in all the observations made on the short axis. There appears to be some

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[2] The TNT crystal lattice has been reported by some investigators (Ref. 5-6) to belong to the orthorhombic system; others (Ref. 7-8) maintain that it is monoclinic. Nomenclature for the crystallographic axes in these two systems is different. Work is currently in progress by others in this Laboratory to determine definitely the crystal structure, but until this is completed it appears advisable to refer to the crystallographic axes of TNT as the short, intermediate and long axes.

TABLE 3

Thermal Expansion Data for α-TNT

| TNT Specimen | Length $l$ (in.) | Temp. Range $\Delta t$ (°C) | Galv. Defln. $D$ (cm) | Coefficient of Expansion × $10^6$ $E$ (in./in./°C) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Short Axis | | Intermediate Axis | | Long Axis | |
| | | | | Heating | Cooling | Heating | Cooling | Heating | Cooling |
| (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) | (9) | (10) |
| Crystal 1 | | | | | | | | | |
| Short Axis | 0.148 | 23.5–53 | 24.8 | 181 | -- | -- | -- | -- | -- |
| Inter. " | .584 | 22–59.5 | 24.9 | -- | -- | 50.5 | -- | -- | -- |
| Long " | .769 | 23–54 | 26.5 | -- | -- | -- | -- | 49.3 | -- |
| Crystal 2 | | | | | | | | | |
| Short Axis(1) | .126 | 22.5–70.5 | 27.7 | 187 | -- | -- | -- | -- | -- |
| " " (2) | .126 | 26–73 | 26.2 | 173 | -- | -- | -- | -- | -- |
| Inter. " (1) | .342 | 23–73 | 19.3 | -- | -- | 50.0 | -- | -- | -- |
| " " (2) | .330 | 22.5–69.0 | 17.7 | -- | -- | 51.0 | -- | -- | -- |
| Long " (1) | .431 | 26.5–72 | 21.9 | -- | -- | -- | -- | 45.7 | -- |
| " " (2) | .424 | 28–74 | 24.3 | -- | -- | -- | -- | 43.9 | -- |
| Crystal 3 | | | | | | | | | |
| Long Axis (1) | .452 | 27–72 | 22.8 | -- | -- | -- | -- | 49.8 | -- |
| " " (2) | .448 | 21–72 | 18.85 | -- | -- | -- | -- | 36.6* | -- |
| " " (3) | .448 | 76–32 | 24.9 | -- | -- | -- | -- | -- | 55.9* |
| Crystal 4 | | | | | | | | | |
| Inter. Axis | .395 | 21–72 | 22.45 | -- | -- | 49.5 | -- | -- | -- |
| " " | .390 | 72–30 | 22.1 | -- | -- | -- | 59.0* | -- | -- |
| Crystal 5 | | | | | | | | | |
| Short Axis(1) | .1135 | 22.5–79 | 26.3 | 181 | -- | -- | -- | -- | -- |
| " " (2) | .1132 | 79.5–29 | 26.3 | -- | 204 | -- | -- | -- | -- |
| Crystal 6 | | | | | | | | | |
| Short Axis(1) | .1255 | 23.5–72 | 24.6 | 179 | -- | -- | -- | -- | -- |
| " " (2) | .1255 | 26.5–76 | 26.7 | 181 | -- | -- | -- | -- | -- |
| | | 76–23 | 30.6 | -- | 206 | -- | -- | -- | -- |
| Crystal 7 | | | | | | | | | |
| Short Axis(1) | .1306 | 24–78 | 28.9 | 181 | -- | -- | -- | -- | -- |
| " " (2) | .1306 | 78–28 | 30.0 | -- | 204 | -- | -- | -- | -- |
| " " (3) | .1299 | 22–78 | 25.5 | 155* | -- | -- | -- | -- | -- |
| " " (4) | 0.1299 | 78–31 | 25.0 | -- | 181* | -- | -- | -- | -- |
| *Average* | | | | *181* | *204* | *50.2* | -- | *47.2* | -- |

* Not included in average values.

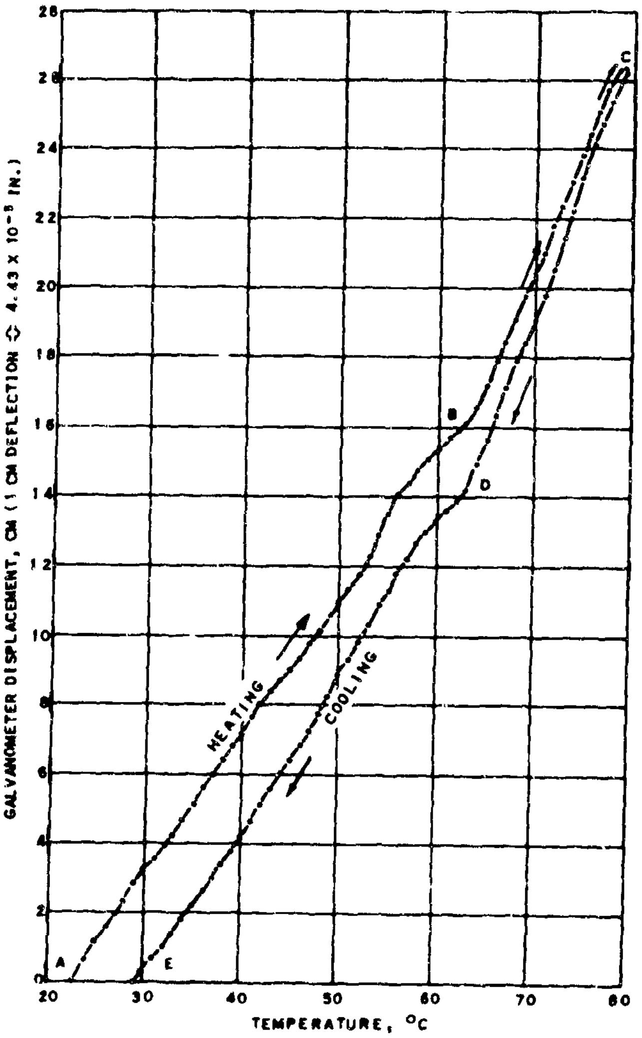

Fig. 3. Length Changes of Alpha-TNT Along the Short Axis. $L$ = 0.1135 in.

correlation between the previous heat treatment of the sample crystal and its expansion behavior. In Fig. 4 some inflections may be observed in the first heating and cooling curve, but very pronounced inflections occur in the neighborhood of 55°C on the second heating and cooling curve, which was obtained without removing the sample from the apparatus.

No such break was as pronounced in the expansion curves for either the intermediate or long axes of TNT (Fig. 5 and 6), although slight inflections were sometimes detected. The cooling curve for the long

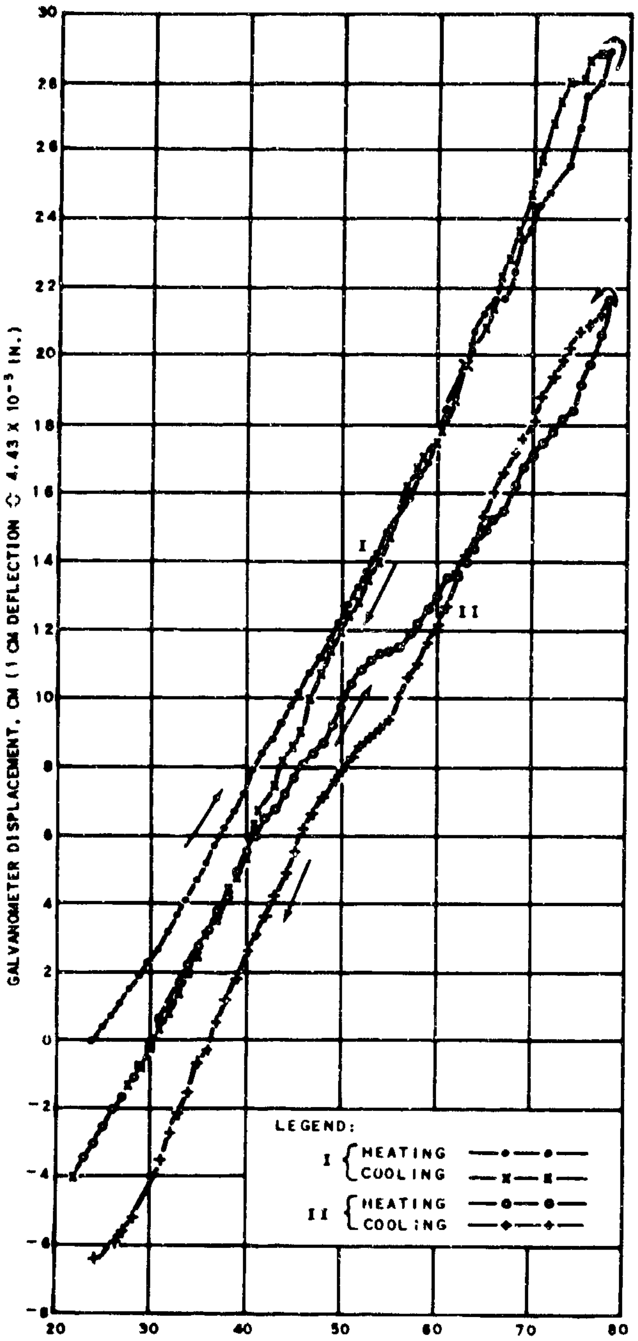

Fig. 4. Effect of Previous Heating on Length Changes of Alpha-TNT Along the Short Axis. $L = 0.130$ in.

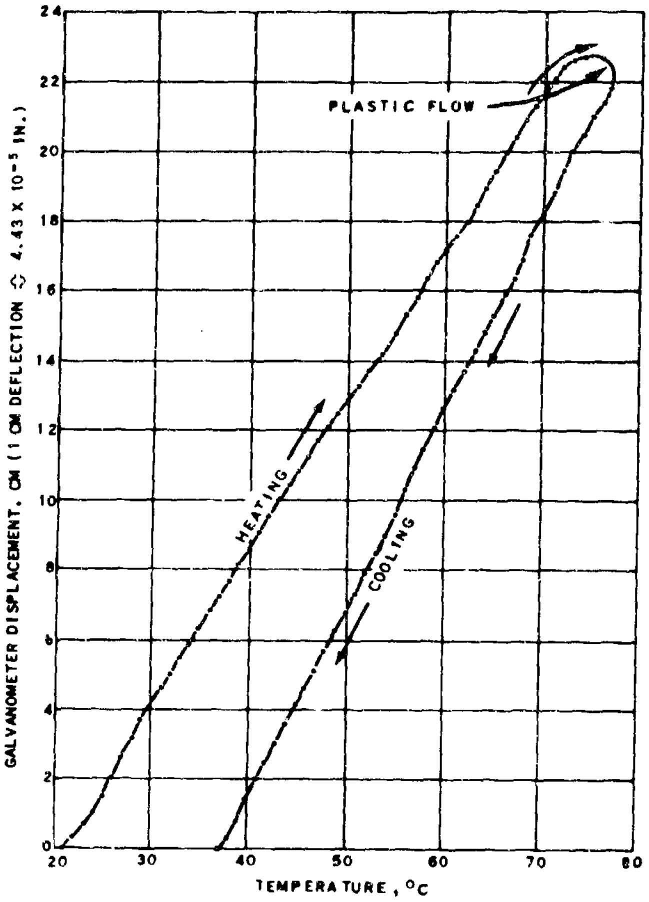

Fig. 5. Length Changes of Alpha-TNT Along the Intermediate Axis. $L$ = 0.395 in.

axis indicates that a gradual change in slope might occur in the neighborhood of 64°C.

A phenomenon was noted, however, for both these axes that was not observed for the short one. This was a state of plastic flow, which was evident 8° or 9°C below the melting point and was illustrated by the leveling off and rounded portions at the top of the graphs (Fig. 5 and 6) starting at about 73°C. This behavior is confirmed by the decrease in length, as shown in Table 3, measured for consecutive tests on the same specimen. Also, the original ground surfaces were observed to have become glazed during heating. The amount of plastic flow is greatly increased when the temperature is raised from 79° to 80°C (the dashed portion of the curve in Fig. 6) and length changes almost equal to those for the entire preceding temperature rise (50°C) result.

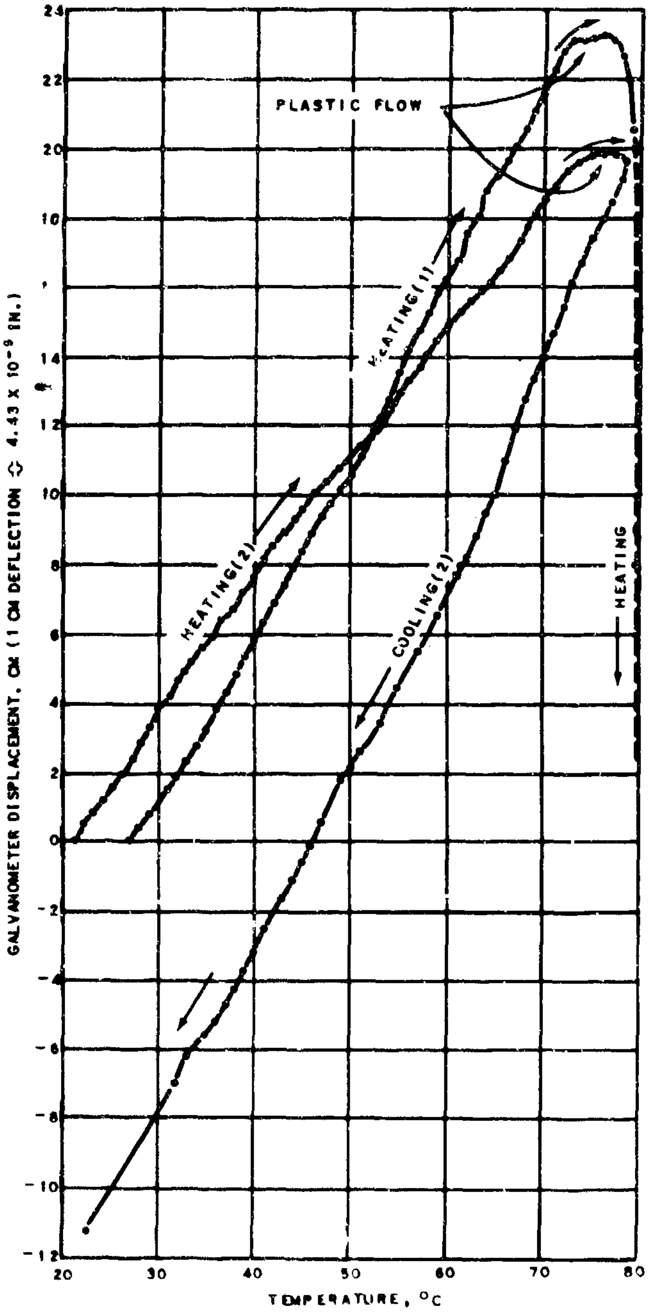

Fig. 6. Length Changes of Alpha-TNT Along the Long Axis. $L$ = 0.452 in.

Further observations, for which no explanation is currently possible, may be made on the data shown in Fig. 4. One is the hysteresis in the cooling curves apparent above 65° to 70°C. This has been noted in other determinations (crystal 6) but is not found in the data obtained on crystal 5 (Fig. 3). The only difference that exists is that the thermal expansion measurements on crystals 6 and 7 were made about 9 months after the crystals had been produced, while only 3 months had elapsed between production and measurement of crystal 5. A second unexplained observation is the apparent irreversible shrinkage obtained on temperature cycling in the absence of plastic flow. This is illustrated in Fig. 4. Finally, the thermal history of the sample is shown to be of importance in its expansion behavior, since rather wide variations were obtained in the coefficient of expansion on a review of two samples. This was noted along the short axis of crystal 7 and along the long axis of crystal 3.

In order to ascertain the manner in which TNT crystals fracture when subjected to thermal shock and correlate this with observed thermal expansions, the following experiments were performed. Large crystals of TNT were grown from the melt on a microscope slide with the short axis perpendicular to the plane of the slide and the long axis parallel to it. The slide was maintained for a time at 75° to 80°C and then plunged into a bath of ice water. As was expected upon cooling, contraction along the short axis was about four times that along the long axis and the crystals were thereby subjected to lengthwise tension with resulting fracture (Fig. 7).

It was considered possible that, since an inflection was observed in the expansion curve for one orientation of TNT, an energy change or polymorphic inversion might also occur. Heating curves were determined, therefore, in an apparatus for the determination of specific heats. Initial heating rates of 8°C per hour were employed and gradually decreased to about 1° or 2°C per hour in the temperature interval 70° to 80°C. By this means detection of energy changes as low as 2.5 calories within the 10-g sample was possible. No inflections were observed over the temperature range (25°-80°C) investigated. From this it can be concluded that either no phase change had occurred or that, if one had, it involved an extremely small energy change or occurred at a sluggish rate.

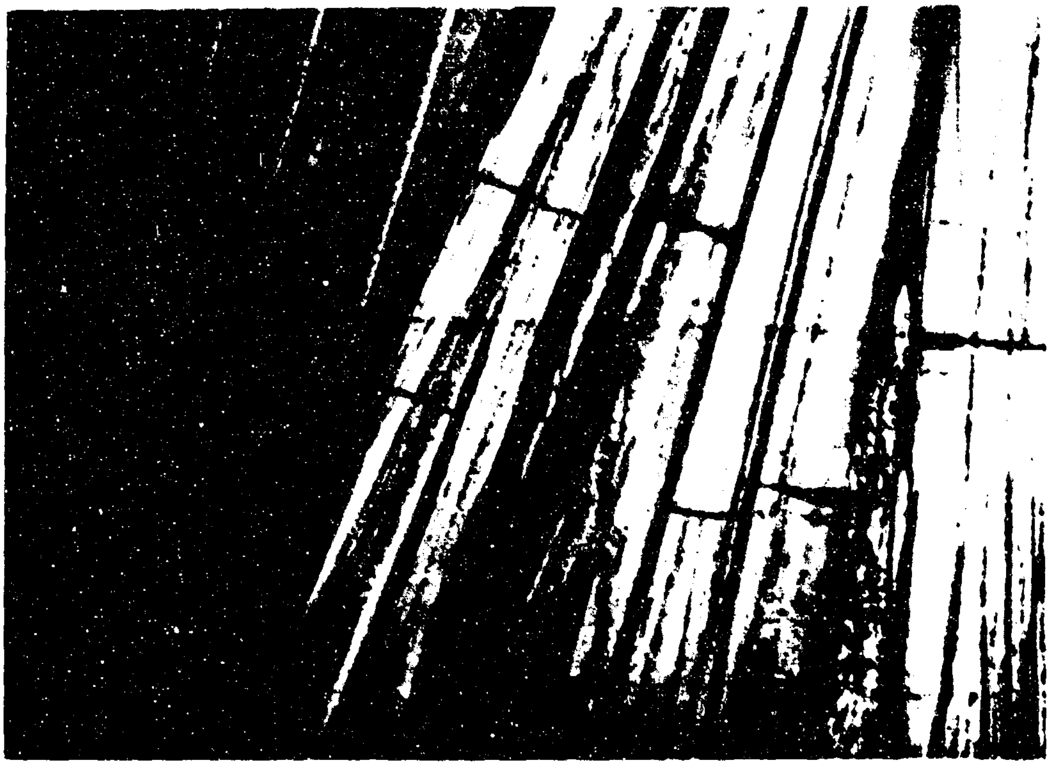

Fig. 7. Photomicrograph of TNT Crystals on a Microscope Slide, Thermal-Shocked From 75°C Into Ice Water (× 84).

*SAMPLE CALCULATIONS*

The displacement corresponding to each centimeter of galvanometer deflection is calculated from the following formula:

$$K = \frac{lE\Delta t}{D - C\Delta t}$$

where

$K$ = calibration constant
$l$ = length
$E$ = expansion coefficient
$D$ = galvanometer deflection
$C$ = correction
$\Delta t$ = temperature interval
$D - C\Delta t$ = net galvanometer deflection

For example, in determination 1 under electrolytic copper (Table 2) the calibration constant is found as follows:

$$K = \frac{1.014 \text{ in.} \times 16.98 \times 10^{-6} \text{in./in./°C} \times 46°\text{C}}{21.1 \text{ cm} - (0.06 \text{ cm/°C} \times 46°\text{C})}$$

$$= 4.32 \times 10^{-5} \text{ in./cm deflection}$$

The coefficient of thermal expansion for TNT is calculated from the calibration constant, *K*, (Table 2) and the data given in Table 3, employing the formula

$$E = \frac{KD}{l\Delta t}$$

For example, in determination 1 under crystal 1 (Table 3) the expansion coefficient is found as follows:

$$E = \frac{4.43 \times 10^{-5} \text{ in./cm} \times 24.8 \text{ cm}}{0.148 \text{ in.} \times 29.5°\text{C}}$$

$$= 181 \times 10^{-6} \text{ in./in./°C}$$

## DISCUSSION

The significance of high coefficients of expansion for TNT—a much higher expansion along one crystallographic axis than along the others, and a nonuniform expansion along that axis—is that the crystal will have anisotropic physical properties. This explains to a large extent the sensitivity of TNT to temperature changes, its low mechanical strength, and variation in other physical properties under certain conditions of storage. The wide variation in expansion is likely to introduce appreciable strains in the crystal lattice of TNT crystals formed from the melt. The relief of such strains may take several courses. If the stresses causing the strains are sufficiently large, fracture results, as in the thermal-shocked crystals shown in Fig. 7. When fracture does not occur, and to some extent when it does, long periods of time may be required for relief of residual strains. This strain relief may take place in different ways, such as delayed fracture, change in dimensions of the crystal, or grain growth.

The behavior of plastic flow along two crystallographic axes of TNT at temperatures considerably below the melting point may indicate that the crystal lattice is not only sometimes strained but also metastable even when essentially strain free. The crystals on which plastic flow was observed were grown from benzene solution at 30°C and at the outset presumably contained a minimum of strains, but some may have been introduced during the heating process. Apparently some mobility or rearrangement along two axes results at an energy state below that for complete melting; whereas, there appears to be no rearrangement along the third axis.

Data reported in the literature for specific heat and thermal conductivity were studied for possible irregularities that might be related to the expansion observations. Prentiss (Ref. 9) determined mean specific heats and thermal diffusivities for TNT in 1923 by the method of mixtures employing liquid air. Unfortunately he was not interested in determinations above room temperature. It is interesting to note, however, that he considered irregularities in specific heat values immediately below the melting point to be a likelihood. Mention was made that possibly incipient melting below the true melting point could occur. It was pointed out that the values determined for specific heat of TNT showed considerable variation from the idealized case of Kopp's law, which states that the molecular heat of a compound is equal to the sum of the atomic heats of the elements composing it.

The Russian workers Belajev and Matushko (Ref. 10) also conducted some studies involving specific heats and thermal conductivities of explosives including TNT. No great accuracy was claimed for the results obtained and the temperature functions were not investigated.

Taylor and Rinkenbach (Ref. 11), employing a liquid oxygen calorimeter, determined mean specific heats between -182.8° and 0°, 20.2°, and 79°C, respectively. From these data an equation was derived and used to calculate specific heats at 10° intervals from 0° to 80°C. Neither this method nor the two previously described are conducive to detecting inflections in specific heat–temperature curves. It appears likely, however, from the two heating curves obtained in the present study that no significant change in specific heat results below the melting point.

A very plausible explanation for the inflections observed in the expansion curves is that they may be due to the interconversion of polymorphic forms. Contrary to the statement in the recent literature (Ref. 6) that no evidence exists for polymorphism in TNT, polymorphism is definitely indicated by X-ray diffraction data obtained in this Laboratory. Evidence has been obtained of the existence of two orthorhombic and one monoclinic modification but, of more importance, this work has demonstrated that some form of disorder exists in crystals prepared under the usual conditions. Changes in the crystal structure involving polymorphic conversions and disorder may well account for the variations in expansion measurements observed.

Further work is necessary before adequate explanations for the phenomena reported herein are available. Such work is underway in connection with a comprehensive program on the crystallography of TNT and a determination of its physical properties and solid state phenomena.

## CONCLUSIONS

The high values for expansion coefficients, the variation in expansion with crystallographic axis, and the nonuniform expansion along a particular axis impart anisotropic physical properties to TNT crystals. Lattice distortion, depending upon the thermal history of a crystal, causes abnormal behavior resulting from alteration of physical characteristics. The nonuniform thermal expansion observed in this work may be evidence for a phase change occurring in TNT between room temperature and its melting point.

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