SINGLE CRYSTAL PEROVSKITES AS ELECTROOPTICALLY ACTIVE MATERIALS

FIRST QUARTERLY PROGRESS REPORT

JULY 1 to OCTOBER 1, 1966

CONTRACT NO. AF 33(615)-5410

Sponsored by: Air Force Material Laboratory
Research and Technology Division
Air Force Systems Command
United States Air Force

UNION CARBIDE CORPORATION
ELECTRONICS DIVISION

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ABSTRACT

A two year research and development program on electrooptically active perovskite crystals ~~has been~~ initiated. The program consists of three parts; growth improvement of potassium tantalate niobate (KTN) crystals, development of new complex perovskite compounds and electrooptical evaluation of these crystals. An improvement in the reproducibility and quality of KTN crystals ~~has been~~ realized, ~~during the period~~. A literature search for complex perovskite compounds and a computer program to generate the formulas and unit cell sizes for all possible complex perovskites are both ~~well~~ underway. Special methods for measuring the required electric, and electrooptic properties of crystals ~~have been~~ previously developed and can now be used for studying the behavior of KTN crystals.

INTRODUCTION:

This report is the first quarterly progress report on Contract No. AF 33(615)-5410. The object of this program is to develop electrooptically active perovskite crystals so that they are suitable for use in laser technology. Of the presently known perovskite crystals, the single crystal solid solution potassium tantalate niobate (KTN) appears to be the best suited for electrooptical applications because the Curie temperature can be adjusted to be near room temperature. Accordingly, a specific objective of the present program is to solve the materials problems in KTN. This development of KTN represents approximately half of the total effort on this contract. The problems in making electrooptically perfect crystals of KTN are severe, however, and many are apparently inherent characteristics of solid-solution single crystals. Stoichiometric compounds are usually more homogeneous than are solid solutions. The remainder of the effort has been devoted to a systematic search for complex perovskite compounds that would be suitable as electrooptic elements. Before either type of perovskite can be considered as a suitable electrooptic element, its electrical, optical and electrooptical behavior must be known in considerable detail. A considerable effort has, therefore, been devoted toward the establishment of laboratory evaluation methods which have already proven to be a great aid in evaluating crystals of KTN. Since the program is naturally divided into three segments (growth of KTN crystals, complex perovskite compounds and crystal evaluation), this report is similarly divided.

During the present quarter, work progressed on all three phases of the problem. Much of this work represented a continuation of studies and process development that was underway before the inception of the contract. In particular, we have been growing KTN for more than a year. Many problems were evident, but their cause and cure was more elusive, partly because of variation from run to run. The prime objective during this quarter has been to develop a reproducible process that would produce crystals of consistent quality. This objective has been largely satisfied. The study of complex perovskite compounds is, however, new to us, and this aspect of the program has been divided into two general chores, a literature survey and a computer program. Both jobs are still in progress but are well underway. The development of evaluation methods has also been a continuation of pre-contract efforts. We are now well equipped for measuring electrical, optical and electrooptical properties by novel rapid methods which we have developed. We can now devote most of our attention to evaluation of KTN crystals rather than methods development.

SUMMARY:

The quality and reproducibility of KTN crystals has been improved by more careful control of the growth variables. The excess of K_2O, required to eliminate cloudiness, has been reduced from about 20 percent to 4 percent by weight, with no deleterious effect. Routine additions of K_2O, to compensate for losses by volatilization, also decreased the variability of the Curie point. The establishment of proper thermal gradients in the melt has eliminated need for mechanical stirring, while maintaining or improving crystal quality. Returning to slower pull-rates has also improved quality. No alteration of the optical strain pattern has been observed in annealing experiments, but there is evidence that polishing strains can be removed by chemical etching. Attempts to pull crystals along directions other than $\langle 100 \rangle$ invariably produce poorer crystals.

The rules of valence and stereochemistry have been formulated so that complex perovskite compounds can be systematically organized. The free-ion data for 95 elements have been collected; these data are the input information for the computer programs. Five basic computer programs have been written in FORTRAN-IV. These treat compounds with "multiplicities" of 1 to 3 and a total number of cations of 2 to 4. The computer program tests all combinations for valence and size compatibility with the perovskite structure and outputs the average ionic radii, unit cell edge and tolerance factor for those that pass. Initial tests show that there are several thousand potential compounds. More selection rules are being devised in order to limit the number of compounds.

A literature search of Chemical Abstracts, for formulas and other data on actual complex perovskites, is nearly complete. This will be combined with previous lists and cross-correlated with the computer-generated compounds.

Laboratory procedures and the equipment needed for accurate measurements of electric and electrooptic properties of crystals have been developed. These include means for measuring the linear and nonlinear dielectric properties, the Curie-Weiss temperature dependence of the susceptibility, and the quadratic electrooptic coefficients. Other parameters of interest such as the optical transmission, extinction ratios and natural or strain birefringence may also be measured. The equipment may also be used for study of electrooptic modulation and light switching. These procedures are illustrated by measurements made on a crystal of KTN that is representative of the "state of the art" at the end of the first quarter.

POTASSIUM TANTALATE NIOBATE (KTN):

Prior to this report period, it had proved very difficult to produce good KTN crystals on a reproducible basis. Growth was carried out in two large Globar furnaces which provided heating zones having low thermal gradients, thus requiring mechanical stirring to insure a homogeneous melt. Up to 20 weight percent of excess K_2O was added to the melts in order to improve crystal clarity. Ta:Nb ratios were varied from melt to melt so that the Curie temperature (T_c) varied greatly from crystal to crystal. Likewise, several crystals were often grown from the same melt with no additions being made to the melt after each pull, thus causing a large variation of T_c from crystal to crystal due to the gradual depletion of Ta_2O_5 from the melt. This depletion results from the great difference in the composition of the crystal from that of the melt.

At the beginning of this investigation, we undertook a basic approach for the growth of KTN designed to clear up such points as: 1) the need for excess K_2CO_3 in the melt; 2) variation of T_c with Ta:Nb ratios in the melt composition; 3) alteration of growth conditions so that mechanical stirring could be eliminated; 4) optimum growth rates; and 5) the effect of seed orientation on crystal quality.

It was desired to grow crystals having a T_c near room temperature, or slightly below room temperature A melt composition of $KTa_{0.32}Nb_{0.68}O_3$ produces crystals having a composition of $KTa_{0.63}Nb_{0.37}O_3$ and which have a T_c near 10°C. The crystals were cloudy if no excess K_2O was added to the melt, but only 4 weight percent was needed to eliminate cloudiness, a large reduction from the 20 percent previously used. K_2O was found to volatilize from the melt at a rate of one gram per day. A practice which has been adopted is to replenish the melt after each growth with KTN powder having the same weight and composition as the pulled crystal as well as adding enough K_2O to compensate for volatilization losses. This has resulted in a large reduction of the variability of T_c from crystal to crystal.

Growth conditions in the Globar furnaces were altered so as to provide a large vertical thermal gradient in the melt. This gradient provides active stirring of the melt, so that mechanical stirring is no longer needed. In addition, several growths were carried out in gas stations, in which the crucible is supported by a ceramic pedestal and is heated from the bottom by an oxy-hydrogen flame. Both vertical and radial thermal gradients in this system are very steep so that thermal stirring in the melt is active. Several crystals contained optically clear areas, but when these areas were sectioned away from the crystals, they were found to be highly strained when viewed between crossed polaroids. This was due to the fact that in order to achieve growth on the seed, it was necessary to impose a severe thermal gradient upon the crystal during growth.

In the past, a growth rate of 0.01 inch/hour had been found to result in optimum crystal quality. We undertook a new study to see if faster pull rates could be used. Pull rates of up to 0.1 inch/hour were used, with rates in the range of 0.02 - 0.03 inch/hour producing the most satisfactory results. KTN grows with a very flat interface when ⟨100⟩ seeds are used, so that at rates faster than 0.03 inch/hour, the crystal pulls out of the melt easily.

A series of annealing experiments were carried out in order to determine whether or not crystal strain could be removed by thermal treatments. Crystals were annealed at temperatures of 1050, 1090, and 1150°C for periods up to 48 hours. No changes in the strain patterns were observed. One of the areas which will be investigated in the next report period is the possible removal of strain by chemical polishing techniques. There is evidence that much of the crystal strain observed between crossed polaroids is caused by mechanically polishing the crystal faces, so that this strain could be removed by chemical polishing.

All growths were carried out using ⟨100⟩ seeds with two exceptions, in which ⟨111⟩ seeds were used. In both cases, the ⟨111⟩ crystals had a very high inclusion content, much higher than generally observed for ⟨100⟩ crystals. Instead of growing with a flat growth interface as in the case of ⟨100⟩ crystals, ⟨111⟩ crystals grow with multi-facets which protrude into the melt, thus offering many more nucleation sites and increasing the chances for inclusion of secondary phases.

No relation has been noted between seed quality and corresponding crystal quality. This will receive more attention in coming months.

COMPLEX PEROVSKITE COMPOUNDS:

The general objective in studying complex perovskite compounds is to find new compositions that have dielectric and optical properties similar to KTN but which are stoichiometric compounds. Such compounds should permit growth of single crystals of greater uniformity and homogeneity than possible with solid solutions. Many complex perovskites, both solid solutions and compounds, have been prepared, as shown below. We may represent such compositions by the general chemical formula:

$$\left(A_i\right)_{m_i}\left(B_j\right)_{n_j} O_{3p} \qquad (1)$$

where A_i and B_j each represent collectively all the ions that occupy the A-site and B-site respectively, in the usual perovskite structure ABO_3. The letters m, n and p are integral atmoic-ratio numbers for each element, as in the usual chemical symbolism. Stoichiometry, in the perovskite structure, requires:

$$\sum_i m_i = \sum_j n_j = p \qquad (2)$$

Furthermore, if the valence of the A_i atom is represented by v_i and that of B_j by w_j, we must also have:

$$\sum_i v_i\, m_i + \sum_j w_j\, n_j = M + N = 6p \qquad (3)$$

These rules apply to solid solutions as well as stoichiometric compounds. Solid solutions occur when different elements having the same valence substitute in the same site. In solid solutions, the m or n values need not be integral. Here we consider only stoichiometric compounds where m and n are integral.

Since one can have many different types of compounds that satisfy the rules, it is convenient to group them according to the following indices:

1) The multiplicity, p. This number is one-third the number of oxygen atoms in the chemical formula when it is written in the usual manner with smallest whole number subscripts.

2) The total number of different cations present, TC. This is equivalent to:

$$TC = \sum_i (1) = \sum_j (1) \qquad (4)$$

3) The two "valence sum" numbers, M and N where:

$$M = \sum v_i\, m_i \qquad M + N = 6p$$

$$N = \sum w_j\, n_j$$

4) The usual chemical formula.

This type of classification is particularly useful in generating computer programs as shown in the following.

(a) Computer Program for Generating Complex Perovskite Compounds:

The present computer programs are based on the rules of stereochemistry and the properties of free ions. The ion name, the valence of the ion and the ionic radius are the input data. It is thus presumed that the necessary properties of the final compound can be calculated from these free ion properties. (Later other information will be incorporated into the program.) The free ion data has been obtained from Ahrens[1]. The ionic radii are for 6-coordination, the radius is increased by 9 percent as by Pauling[2]. The stereochemical rules were adopted from rules developed by others, in particular Roth[3].

Five basic computer programs have been written to deal with different values of the multiplicity, p, and total number of cations, TC. These programs then produced outputs which are ordered according to the values of M and N and then according to the chemical formula. The ions are ordered according to valence of the individual ion, i, j, k, l ....., and secondly according to increasing values of the atomic numbers, Z. The five basic programs are:

1) $p = 1$, $TC = 2$, ABO_3

2) $p = 2$, $TC = 3$, $A_2BB'O_6$ or $AA'B_2O_6$

3) $p = 2$, $TC = 4$, $AA'BB'O_6$

4) $p = 3$, $TC = 3$, $A_3B_2B'O_9$ or $A_2A'B_3O_9$

5) $p = 3$, $TC = 4$, $A_2A'B_2B'O_9$

The first four programs treat all possibilities but the fifth is confined to compounds that have no more than two ions per site.

In the actual programs, the ion data, for the ions being considered, is read in and stored in a two dimensional matrix. The first index in this matrix is the valence of the ion, the second is merely an ordering number wherein the ions are listed in increasing atomic number. The program then prints out this matrix so that the ions considered are identified. Next, the program selects ions for the A-site and tests them, selects ions for the B-site and tests them, tests the valence combinations and all the size rules and finally outputs the compounds that pass the tests. (In more recent programs, we first adjust the valences, M and N, then the individual ion valences and the individual ions.) The size rules are as follows, where r_A refers to the radius of any A-ion and $\bar{r}_A$ refers to the average radius of all A-ions:

1. $r_A \le 1.48\text{Å}$
2. $0.97\text{A} \le \bar{r}_A \le 1.35\text{Å}$
3. $r_B \le 1.06\text{Å}$
4. $0.51\text{Å} \le \bar{r}_B \le 1.00\text{Å}$
5. $r_A \le 0.50\, r_B + 0.69\text{Å}$
6. $0.85 \le T \le 0.98$

   where T is the well known tolerance factor defined by:

$$T = \frac{\bar{r}_A + r_o}{\sqrt{2}\,(\bar{r}_B + r_o)} \qquad (5)$$

The field defined by these rules is outlined in Figure 1. Several well known simple perovskites are located to show that the field encloses the high dielectric compounds analogous to those we seek. The output of the programs consists of a listing of the compound formula, the atomic numbers (for ordering purposes), the average A and B radii, the unit cell size and the tolerance factor, T.

An example of the computer program for the simple perovskites, p = 1, TC = 2 is shown in this report. Of course, many of the tests are superfluous in this case, but they are generally included since they are required in the more complex cases. The first page shows the actual program in FORTRAN-IV. Unfortunately, the printer uses the A-character symbols instead of the proper FORTRAN symbols. Thus % is equivalent to (and # is equivalent to =, etc. The second output sheet lists the TABLE OF IONS arranged according to valence. The next two pages show the compounds that passed the tests. Almost all known simple perovskites (that are not too distorted) are included. Furthermore, the unit cell edge CELL compares favorably with actual values for compounds. Examples of complex compounds have not been included only because the lists are so long even when all the ions are not included. We are developing further rules to limit the selection before we run these programs with all ions.

(b) Literature Search:

A Chemical Abstract search of the literature from January 1920 to June of 1965 for potential perovskite materials has been completed. For the sake of completeness, only four rules were followed during the first phase of the program:

1. All compounds will contain a whole number of oxygen atoms that must be divisible by three.
2. No compounds with a vacancy in the A or B site will be considered.

3. The general perovskite formula $\left(A_i\right)_{m_i}\left(B_j\right)_{n_j}O_{3p}$, where $\sum_i m_i = \sum_j n_j = P$ will be adhered to.

4. Finally, only the atoms listed in the table below in all their possible valence states will be considered for compound formation.

A large number of compounds was obtained including ABO_3 type oxides, garnets, ilmenites, and pyrochlores, as well as perovskites. Subsequent structure eliminations and elimination of solid solution type perovskites has reduced the list to 1125 compounds which are either confirmed perovskites or compounds which could not be positively eliminated.

Correlation of the complex perovskite compounds found in the literature search with those generated in the computer program will be shown in future reports.

LIST OF IONS

Ag
Al
As
Au
Ba
Bi
Ca
Cd
Ce
Co
Cr
Cs
Cu
Dy
Er
Eu
Fe
Ga
Gd
Ge
Hf
Hg
Ho
I
In
Ir
K
La
Li
Lu
Mg
Mn
Mo
Na
Nb
Nd
Ni
Np
Os
Pa
Pb
Pd
Pm
Po
Pr
Pt
Pu
Ra
Rb
Re
Rh
Ru
Sb
Sc
Sm
Sn
Sr
Ta
Tb
Te
Th
Ti
Tl
Tm
U
V
W
Y
Yb
Zn
Zr

ELECTRICAL, OPTICAL AND ELECTROOPTICAL TESTING:

A special laboratory facility has been established for studying electrooptic crystals. The crystal is mounted in an adiabatic container on an optical bench which permits photographic or photoelectric detection of the light transmitted by the crystal. The electrical driving of the crystal is done with a special harmonic bridge circuit. This equipment permits a direct measurement of the linear and the first two nonlinear electrical coefficients of the crystal. The electrooptic phase retardation pattern may be recorded simultaneously. The operation of this equipment will not be described in detail since it has been written up and will soon appear in the Review of Scientific Instruments under the title "A Harmonic Bridge for Measurement of Nonlinear Electric and Electrooptic Properties of Crystals".

This apparatus has been used to study various samples of KTN crystals. In particular, we have made fairly extensive measurements on a sample of KTN (NF-II-132-WPX1) which has been transmitted to the Air Force Materials Laboratory in accordance with this contract. The original photographs and oscillographs were also transmitted with the crystal. The results of this study are briefly reviewed here.

The low frequency dielectric constant was measured with a General Radio 1610-A Bridge, over a temperature range from 0°C to 40°C. These data are plotted according to the Curie-Weiss law in Figure 2. The Curie-Weiss law is obeyed for temperatures about 15° above the Curie temperature or higher. For this region, the dielectric impermittivity, β°, is given by:

$$\beta^\circ = 0.774 \times 10^6 \, (T-0.6)$$

At temperatures below 15°, there appears to be departure from the Curie Weiss law. The minimum β-value occurs at 5°C and corresponds to a value of relative dielectric constant K' of about 18,000.

Optical transmission photographs of this crystal are shown in Figure 3. Although KTN is ideally isotropic, these photographs show that this crystal (and all others) exhibits an "extinction angle". This behavior will be investigated more throughly in the near future.

Oscillographs of the electrooptic effect are shown in Figure 4. These patterns are the "normal" pattern observed in KTN crystals. A phase retardation proportional to D^2 and a slight "natural" birefringence are characteristic of KTN cut in this direction. A plot of the maxima-minima vs. D^2 for the third of these oscillographs is shown in Figure 5. The effective electrooptic coefficient can be calculated from the slope of this curve from which we obtain:

$$\frac{\epsilon_o}{2}\left(\xi^{\circ}_{11} - \xi^{\circ}_{12}\right) = 0.121 \qquad (6)$$

This value compares reasonably well with prior measurements on KTN where values near 0.140 were obtained.

Finally, this crystal has been used to demonstrate modulation of an optical beam at audio frequencies.

PLANS FOR NEXT QUARTER:

During the second quarter we shall continue the development of KTN crystal growth. We shall attempt to grow KTN crystals in small Pt-wound resistance furnaces where the temperature control should be very good. We are confident that KTN of useable quality can be produced by continued development of our current growth methods.

The literature search will be completed during the next quarter. We hope to be able to assemble this information on punched cards so it can be cross-correlated with the output from the computer program.

The computer program is now being extended by sub-programs that are designed to take into account oxidation-reduction stability of ions, the stability of the parent oxides and their melting points. We shall also make use of more sophisticated equipment which should speed the operations and permit running more complex programs.

We have engaged in an intensive study of the striations and local dielectric and electrooptic behavior in KTN. The results of this study will be presented in a paper before the International Conference on the Characterization of Materials, Pennsylvania State University, November 16-18, 1966. The results of this study will be reported later. We also hope to start studies on the d-c transport behavior of KTN since these properties are of great importance for any application wherein the crystal must be biased.

REFERENCES

1. L. H. Ahrens, Geochimica et Cosomochimica Acta, 2 155 (1952), and 3 1 (1953).

2. L. Pauling, "The Nature of the Chemical Bond", second edition, p. 368, Cornell University Press, N.Y., 1948.

3. R. S. Roth, J. Res. Nat. Bureau Standards, 58 75 (1957).

SAMPLE COMPUTER PROGRAM

```
                        FORTRAN   RUN
$NO MULTIPLY DIVIDE
$INTEGER SIZE #  2
$REAL SIZE #  4
    C
    C       PROGRAM TO LIST AB03 COMPOUNDS     P#1     TC#2
    C
            DIMENSION AS%7,22¤,IN%7,22¤,AR%7,22¤
          1 FORMAT %A3,3X,I3,F6.2¤
          2 FORMAT %6X,2%A4,I2¤,2%6X,I4¤,2%8X,F5.2¤,3%8X,F6.3¤,8X,F6.2¤
          3 FORMAT %1H1,4X,16HCHEMICAL FORMULA,3X,6HAT # A,4X,6HAT # B,5X,8HA
           1RADIUS,5X,8HB RADIUS,8X,2HCA,12X,2HCB,12X,4HCELL,8X,8HT FACTOR/¤
         45 FORMAT %/50X,10HTHIS IS IT¤
          8 FORMAT %I5¤
            READ %1,8¤ KK
            DO 5 M#1,7
            DO 4 N#1,KK
            READ %1,1¤ AS%M,N¤,IN%M,N¤,AR%M,N¤
          4 CONTINUE
          5 CONTINUE
         47 FORMAT %7%A6,F8.2,6X¤¤
         46 FORMAT %1H1,62X,14H TABLE OF IONS/¤
            WRITE %3,46¤
            DO 48 N#1,KK
            WRITE %3,47¤AS%1,N¤,AR%1,N¤,AS%2,N¤,AR%2,N¤,AS%3,N¤,AR%3,N¤,AS%4,N
           1¤,AR%4,N¤,AS%5,N¤,AR%5,N¤,AS%6,N¤,AR%6,N¤,AS%7,N¤,AR%7,N¤
         48 CONTINUE
            WRITE %3,3¤
            II#0
            DO 6 M#1,4
            DO 7 N#1,KK
            IF%AR%M,N¤¤ 6,6,12
         12 IF%AR%M,N¤.LT.0.97.UR.AR%M,N¤.GT.1.35¤GO TO 7
            I#6-M
            DO 16 J#1,KK
            IF%AR%I,J¤¤ 7,7,14
         14 IF%AR%I,J¤.LT.0.51.OR.AR%I,J¤.GT.1.00¤GO TO 16
            IF%I-3¤ 11,13,11
         13 IF%AR%I,J¤-0.83¤ 11,11,16
         11 CA#1.414*%1.09*AR%M,N¤¤&1.40¤
            CB#2.0*%AR%I,J¤&1.40¤
            CVR#%CA&CB¤/2.0
            T#CA/CB
            IF%T.LT.0.85.OR.T.GT.0.98¤GO TO 16
            IF%AR%M,N¤-%%0.50*AR%I,J¤¤&0.69¤¤ 16,15,15
         15 II#II&1
            IF%II-51¤ 20,21,21
         21 WRITE %3,3¤
            II#1
         20 WRITE %3,2¤AS%M,N¤,M,AS%I,J¤,I,IN%M,N¤,IN%I,J¤,AR%M,N¤,AR%I,J¤,CA,
           1CB,CVR,T
         16 CONTINUE
          7 CONTINUE
          6 CONTINUE
```

SAMPLE COMPUTER PROGRAM

```
                                         TABLE OF IONS
 LI   0.68        MG   0.66        AL   0.51        TI   0.68         V   0.59        CR   0.52        MN   0.46
 NA   0.97        CA   0.99        SC   0.81         V   0.63        NB   0.69        MO   0.62         I   0.50
  K   1.33         V   0.88        TI   0.76        MN   0.60        SB   0.62        TE   0.56        RE   0.56
 CU   0.96        MN   0.80         V   0.74        GE   0.53         I   0.62         W   0.62             0.00
 RB   1.47        FE   0.74        CR   0.63        ZR   0.79        TA   0.68        OS   0.69             0.00
 AG   1.26        CO   0.72        MN   0.66        MO   0.70        BI   0.74         U   0.80             0.00
 CS   1.67        NI   0.69        FE   0.64        RU   0.67        PA   0.89             0.00             0.00
 AU   1.37        CU   0.72        CO   0.63        PD   0.65             0.00             0.00             0.00
 TL   1.47        ZN   0.74        GA   0.62        SN   0.71             0.00             0.00             0.00
      0.00        SR   1.12         Y   0.92        TE   0.70             0.00             0.00             0.00
      0.00        PD   0.80        IN   0.81        CE   0.94             0.00             0.00             0.00
      0.00        CD   0.97        SB   0.76        PR   0.92             0.00             0.00             0.00
      0.00        SN   0.93        LA   1.14        TB   0.81             0.00             0.00             0.00
      0.00        BA   1.34        CE   1.07        HF   0.78             0.00             0.00             0.00
      0.00        PT   0.80        ND   1.04         W   0.70             0.00             0.00             0.00
      0.00        HG   1.10        SM   1.00        RE   0.72             0.00             0.00             0.00
      0.00        PB   1.20        GD   0.97        IR   0.68             0.00             0.00             0.00
      0.00        RA   1.43        DY   0.92        PT   0.65             0.00             0.00             0.00
      0.00             0.00        ER   0.89        PB   0.84             0.00             0.00             0.00
      0.00             0.00        YB   0.86        TH   1.02             0.00             0.00             0.00
      0.00             0.00        TL   0.95        PA   0.98             0.00             0.00             0.00
      0.00             0.00        BI   0.96         U   0.97             0.00             0.00             0.00
```

SAMPLE COMPUTER PROGRAM

CHEMICAL FORMULA	AT # A	AT # B	A RADIUS	B RADIUS	CA	CB	CELL	T FACTOR
K 1 NB 5	19	41	1.33	0.69	4.029	4.180	4.105	0.96
K 1 TA 5	19	73	1.33	0.68	4.029	4.160	4.095	0.97
K 1 BI 5	19	83	1.33	0.74	4.029	4.280	4.155	0.94
K 1 PA 5	19	91	1.33	0.89	4.029	4.580	4.305	0.88
AG 1 NB 5	47	41	1.26	0.69	3.922	4.180	4.051	0.94
AG 1 SB 5	47	51	1.26	0.62	3.922	4.040	3.981	0.97
AG 1 I 5	47	53	1.26	0.62	3.922	4.040	3.981	0.97
AG 1 TA 5	47	73	1.26	0.68	3.922	4.160	4.041	0.94
AG 1 BI 5	47	83	1.26	0.74	3.922	4.280	4.101	0.92
AG 1 PA 5	47	91	1.26	0.89	3.922	4.580	4.251	0.86
CA 2 MN 4	20	25	0.99	0.60	3.505	4.000	3.753	0.88
CA 2 GE 4	20	32	0.99	0.53	3.505	3.860	3.663	0.91
SR 2 TI 4	38	22	1.12	0.68	3.706	4.160	3.933	0.89
SR 2 V 4	38	23	1.12	0.63	3.706	4.060	3.883	0.91
SR 2 MN 4	38	25	1.12	0.60	3.706	4.000	3.853	0.93
SR 2 GE 4	38	32	1.12	0.53	3.706	3.860	3.783	0.96
SR 2 MO 4	38	42	1.12	0.70	3.706	4.200	3.953	0.88
SR 2 RU 4	38	44	1.12	0.67	3.706	4.140	3.923	0.90
SR 2 PD 4	38	46	1.12	0.65	3.706	4.100	3.903	0.90
SR 2 SN 4	38	50	1.12	0.71	3.706	4.220	3.963	0.88
SR 2 TE 4	38	52	1.12	0.70	3.706	4.200	3.953	0.88
SR 2 HF 4	38	72	1.12	0.78	3.706	4.360	4.033	0.85
SR 2 W 4	38	74	1.12	0.70	3.706	4.200	3.953	0.88
SR 2 RE 4	38	75	1.12	0.72	3.706	4.240	3.973	0.87
SR 2 IR 4	38	77	1.12	0.68	3.706	4.160	3.933	0.89
SR 2 PT 4	38	78	1.12	0.65	3.706	4.100	3.903	0.90
CD 2 GE 4	48	32	0.97	0.53	3.475	3.860	3.668	0.90
BA 2 TI 4	56	22	1.34	0.68	4.045	4.160	4.103	0.97
BA 2 ZR 4	56	40	1.34	0.79	4.045	4.380	4.213	0.92
BA 2 MO 4	56	42	1.34	0.70	4.045	4.200	4.123	0.96
BA 2 RU 4	56	44	1.34	0.67	4.045	4.140	4.093	0.98
BA 2 SN 4	56	50	1.34	0.71	4.045	4.220	4.133	0.96
BA 2 TE 4	56	52	1.34	0.70	4.045	4.200	4.123	0.96
BA 2 CE 4	56	58	1.34	0.94	4.045	4.680	4.363	0.86
BA 2 PR 4	56	59	1.34	0.92	4.045	4.640	4.343	0.87
BA 2 TB 4	56	65	1.34	0.81	4.045	4.420	4.233	0.92
BA 2 HF 4	56	72	1.34	0.78	4.045	4.360	4.203	0.93
BA 2 W 4	56	74	1.34	0.70	4.045	4.200	4.123	0.96
BA 2 RE 4	56	75	1.34	0.72	4.045	4.240	4.143	0.95
BA 2 IR 4	56	77	1.34	0.68	4.045	4.160	4.103	0.97
BA 2 PB 4	56	82	1.34	0.84	4.045	4.480	4.263	0.90
BA 2 U 4	56	92	1.34	0.97	4.045	4.740	4.393	0.85
HG 2 TI 4	80	22	1.10	0.68	3.675	4.160	3.918	0.88
HG 2 V 4	80	23	1.10	0.63	3.675	4.060	3.868	0.91
HG 2 MN 4	80	25	1.10	0.60	3.675	4.000	3.838	0.92
HG 2 GE 4	80	32	1.10	0.53	3.675	3.860	3.768	0.95
HG 2 MO 4	80	42	1.10	0.70	3.675	4.200	3.938	0.88
HG 2 RU 4	80	44	1.10	0.67	3.675	4.140	3.908	0.89
HG 2 PD 4	80	46	1.10	0.65	3.675	4.100	3.888	0.90
HG 2 SN 4	80	50	1.10	0.71	3.675	4.220	3.948	0.87

SAMPLE COMPUTER PROGRAM

```
CHEMICAL FORMULA   AT # A   AT # B   A RADIUS   B RADIUS    CA      CB      CELL    T FACTOR

   HG 2  TE 4        80       52       1.10       0.70     3.675   4.200   3.938     0.88
   HG 2   W 4        80       74       1.10       0.70     3.675   4.200   3.938     0.88
   HG 2  RE 4        80       75       1.10       0.72     3.675   4.240   3.958     0.87
   HG 2  IR 4        80       77       1.10       0.68     3.675   4.160   3.918     0.88
   HG 2  PT 4        80       78       1.10       0.65     3.675   4.100   3.888     0.90
   PB 2  TI 4        82       22       1.20       0.68     3.829   4.160   3.995     0.92
   PB 2   V 4        82       23       1.20       0.63     3.829   4.060   3.945     0.94
   PB 2  MN 4        82       25       1.20       0.60     3.829   4.000   3.915     0.96
   PB 2  ZR 4        82       40       1.20       0.79     3.829   4.380   4.105     0.87
   PB 2  MO 4        82       42       1.20       0.70     3.829   4.200   4.015     0.91
   PB 2  RU 4        82       44       1.20       0.67     3.829   4.140   3.985     0.92
   PB 2  PD 4        82       46       1.20       0.65     3.829   4.100   3.965     0.93
   PB 2  SN 4        82       50       1.20       0.71     3.829   4.220   4.025     0.91
   PB 2  TE 4        82       52       1.20       0.70     3.829   4.200   4.015     0.91
   PB 2  TB 4        82       65       1.20       0.81     3.829   4.420   4.125     0.87
   PB 2  HF 4        82       72       1.20       0.78     3.829   4.360   4.095     0.88
   PB 2   W 4        82       74       1.20       0.70     3.829   4.200   4.015     0.91
   PB 2  RE 4        82       75       1.20       0.72     3.829   4.240   4.035     0.90
   PB 2  IR 4        82       77       1.20       0.68     3.829   4.160   3.995     0.92
   PB 2  PT 4        82       78       1.20       0.65     3.829   4.100   3.965     0.93
   PB 2  PB 4        82       82       1.20       0.84     3.829   4.480   4.155     0.85
   LA 3  AL 3        57       13       1.14       0.51     3.737   3.820   3.779     0.98
   LA 3  TI 3        57       22       1.14       0.76     3.737   4.320   4.029     0.87
   LA 3   V 3        57       23       1.14       0.74     3.737   4.280   4.009     0.87
   LA 3  CR 3        57       24       1.14       0.63     3.737   4.060   3.899     0.92
   LA 3  MN 3        57       25       1.14       0.66     3.737   4.120   3.929     0.91
   LA 3  FE 3        57       26       1.14       0.64     3.737   4.080   3.909     0.92
   LA 3  CO 3        57       27       1.14       0.63     3.737   4.060   3.899     0 92
   LA 3  GA 3        57       31       1.14       0.62     3.737   4.040   3.889     0.93
   LA 3  SB 3        57       51       1.14       0.76     3.737   4.320   4.029     0.87
   CE 3  AL 3        58       13       1.07       0.51     3.629   3.820   3.725     0.95
   CE 3  CR 3        58       24       1.07       0.63     3.629   4.060   3.845     0.89
   CE 3  MN 3        58       25       1.07       0.66     3.629   4.120   3.875     0.88
   CE 3  FE 3        58       26       1.07       0.64     3.629   4.080   3.855     0.89
   CE 3  CO 3        58       27       1.07       0.63     3.629   4.060   3.845     0.89
   CE 3  GA 3        58       31       1.07       0.62     3.629   4.040   3.835     0.90
   ND 3  AL 3        60       13       1.04       0.51     3.583   3.820   3.702     0.94
   ND 3  CR 3        60       24       1.04       0.63     3.583   4.060   3.822     0.88
   ND 3  MN 3        60       25       1.04       0.66     3.583   4.120   3.852     0.87
   ND 3  FE 3        60       26       1.04       0.64     3.583   4.080   3.832     0.88
   ND 3  CO 3        60       27       1.04       0.63     3.583   4.060   3.822     0.88
   ND 3  GA 3        60       31       1.04       0.62     3.583   4.040   3.812     0.89
   SM 3  AL 3        62       13       1.00       0.51     3.521   3.820   3.671     0.92
   SM 3  GA 3        62       31       1.00       0.62     3.521   4.040   3.781     0.87
   GD 3  AL 3        64       13       0.97       0.51     3.475   3.820   3.648     0.91
   TH 4  MG 2        90       12       1.02       0.66     3.552   4.120   3.836     0.86

                         THIS IS IT
```

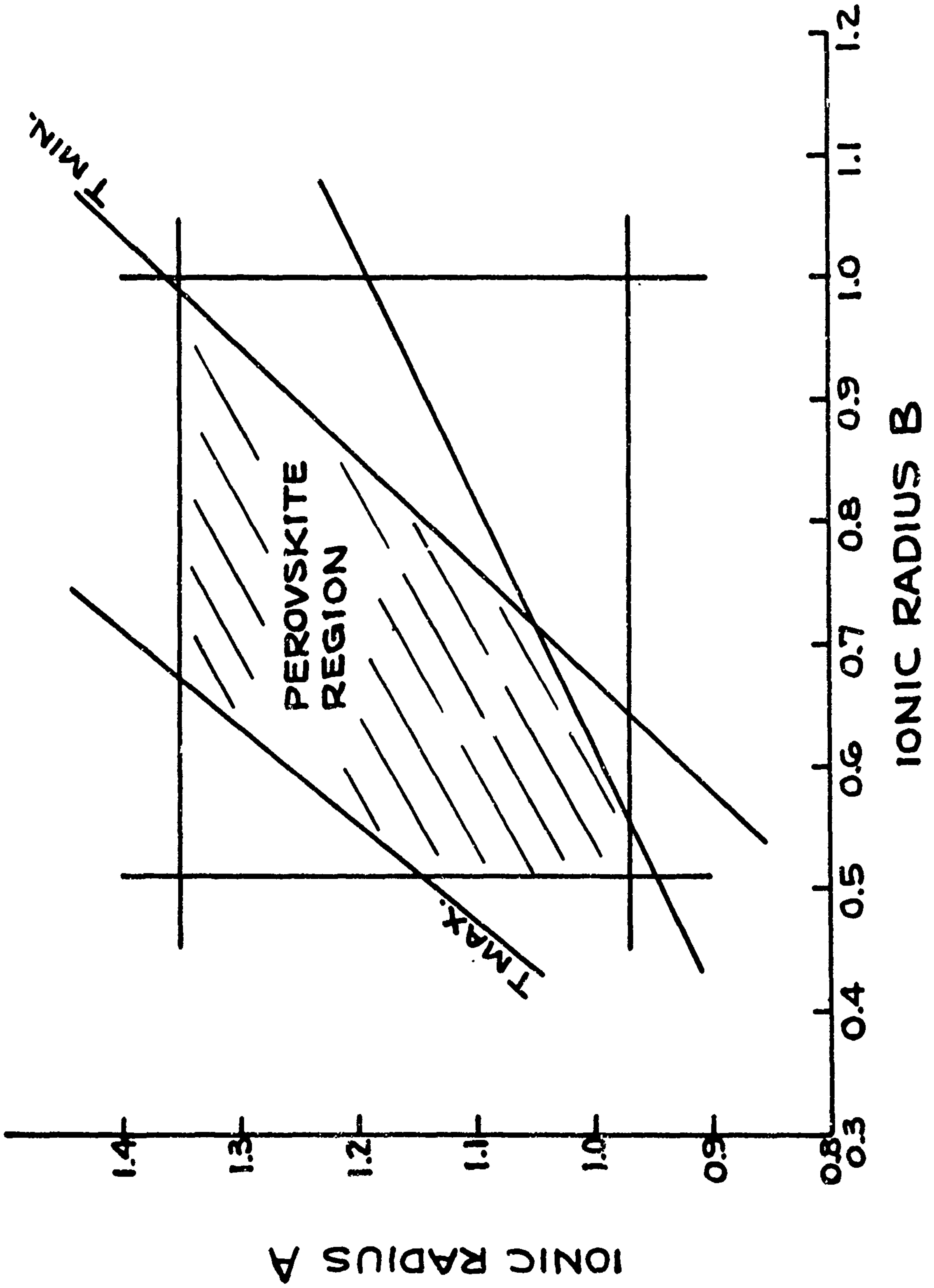

IONIC RADIUS A
1.4
1.3
1.2
1.1
1.0
0.9
0.8
IONIC RADIUS B
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
PEROVSKITE REGION
T MIN.
T MAX.

FIG. 1

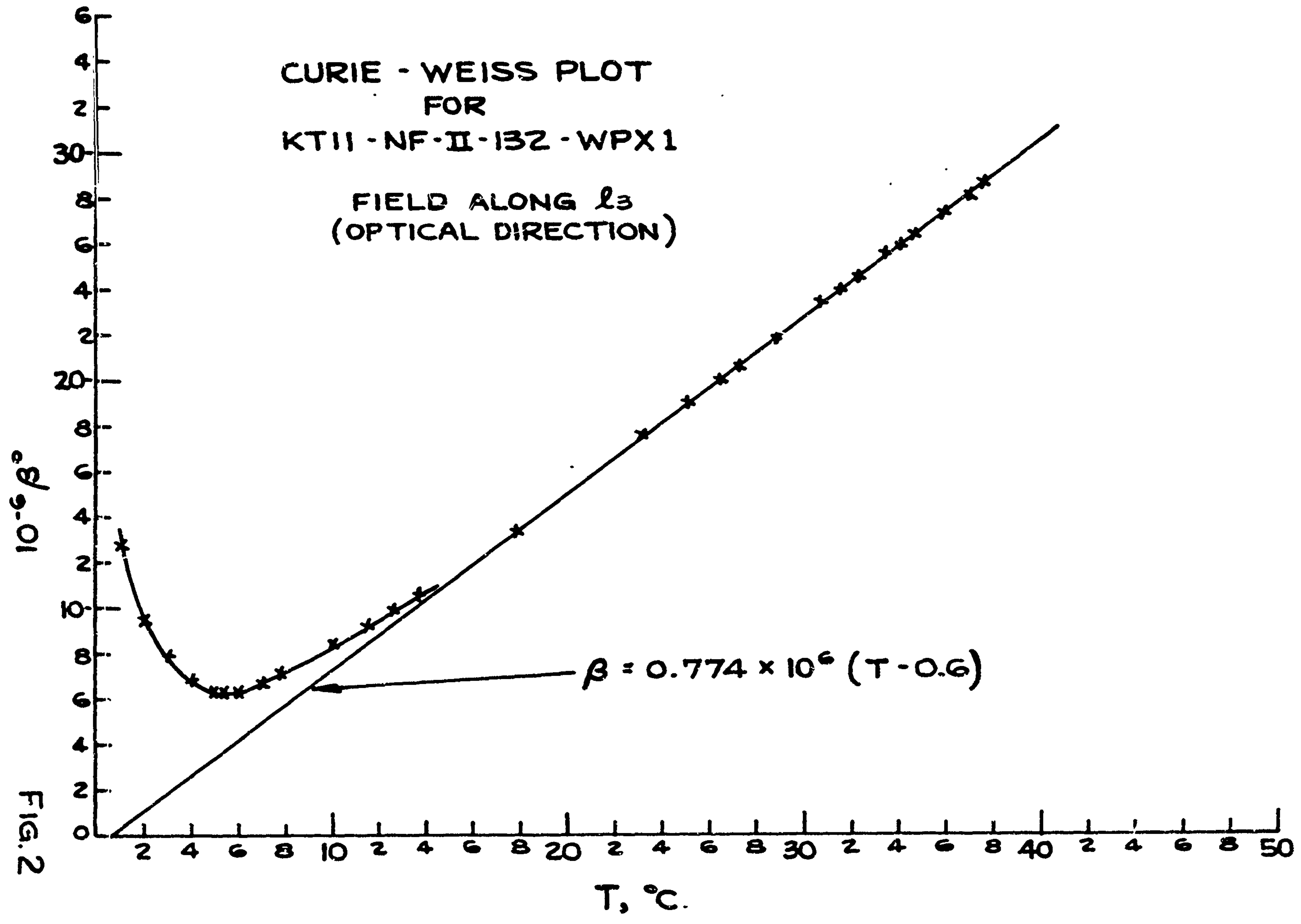

CURIE - WEISS PLOT
FOR
KT11 - NF - II - 132 - WPX1
FIELD ALONG ℓ_3
(OPTICAL DIRECTION)
$\beta = 0.774 \times 10^6 (T - 0.6)$
$10^{-6} \beta^{o}$
6
4
2
30
8
6
4
2
20
8
6
4
2
10
8
6
4
2
0
2
4
6
8
10
2
4
6
8
20
2
4
6
8
30
2
4
6
8
40
2
4
6
8
50
T, °C.

FIG. 2

FIGURE 3

Transmission Photographs of KTN Crystal

NF-II-132

in Polarized Light

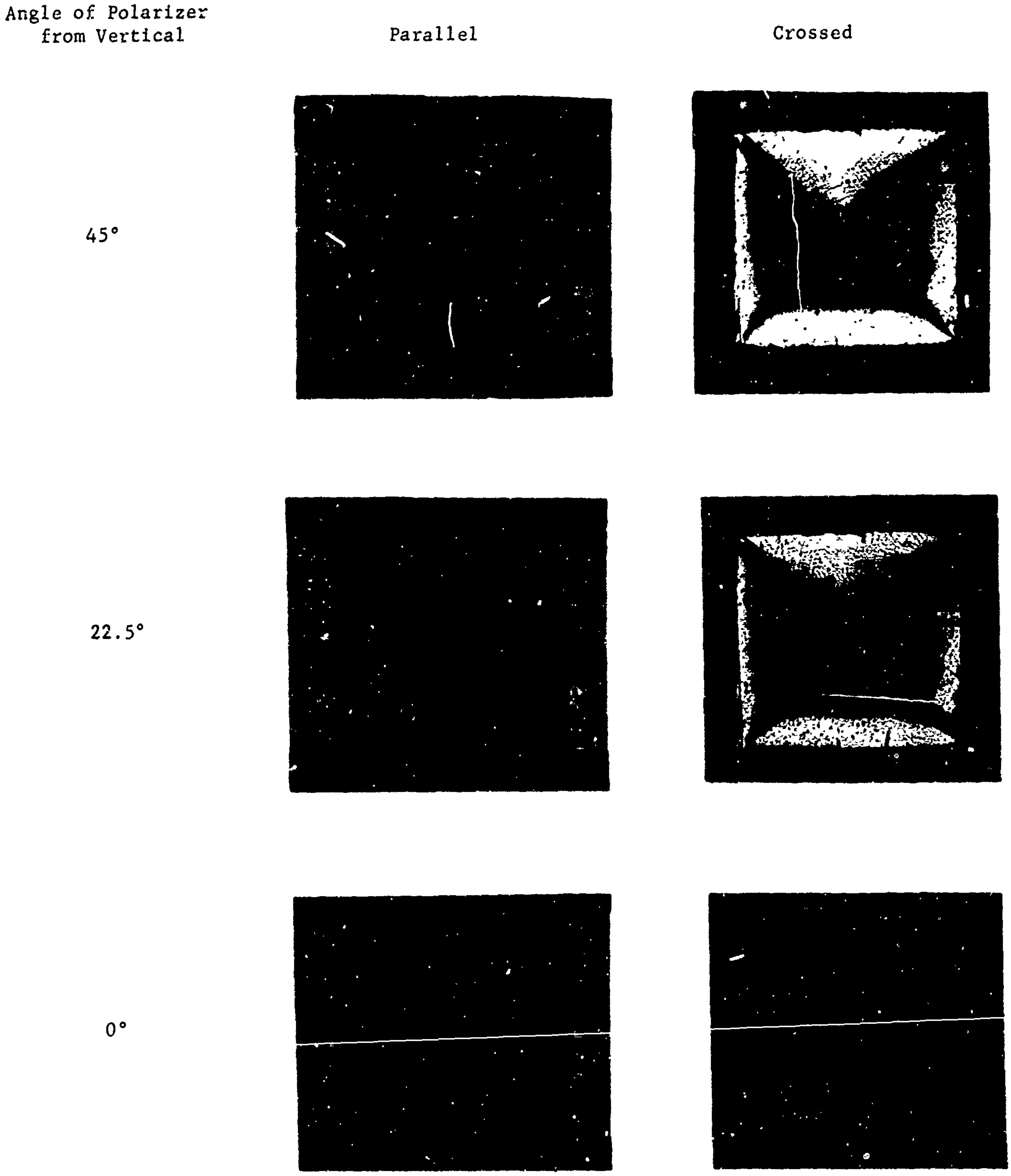


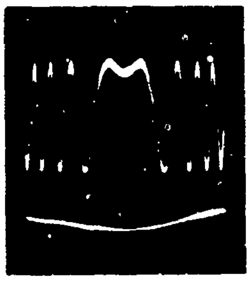
FIGURE 4

Oscillographs of KTN-NF-II-132

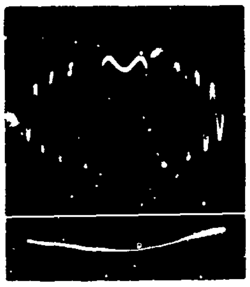
(1 cm horizontal ≙ 0.1μ coulomb)

1 mm aperture at 1:1 magnification
Parallel polarizers at 45°

1 mm aperture at 1:1 magnification
Crossed polarizers at 45°



1 mm aperture at 2:1 magnification
(equivalent to 1/2 mm aperture)
Crossed polarizers at 45°



1 mm aperture at 1:2 reduction
(equivalent to 2 mm aperture)
Crossed polarizers at 45°

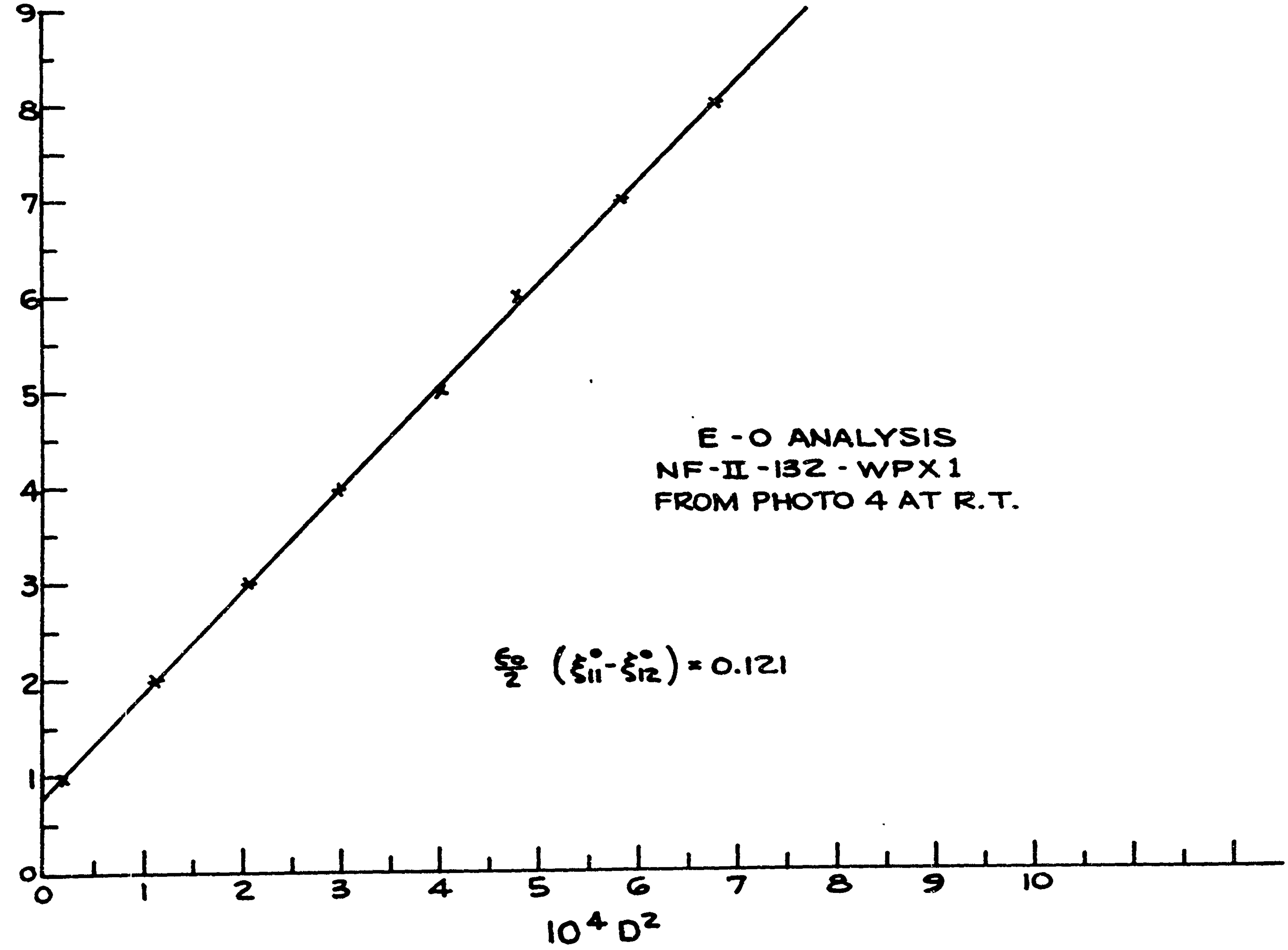

E - O ANALYSIS
NF-II-132 - WPX1
FROM PHOTO 4 AT R.T.
$\frac{\epsilon_0}{2}\left(\xi_{11}^{\circ}-\xi_{12}^{\circ}\right) = 0.121$
$\overline{m}$
0
1
2
3
4
5
6
7
8
9
10
$10^4 D^2$

FIG. 5