

THE PRODUCTION OF LARGE SINGLE
HALIDE CRYSTALS FOR OPTICAL USE

by

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THE GENERAL PROBLEM

The importance of crystal studies has become increasingly apparent as the range of their application has been extended. The present studies of the solid state and physical metallurgy are concerned with crystal structures. The very important discovery of X-ray diffraction has given impetus to this work.

Large single crystals of various substances are required for the study of their various properties. Optical instruments, for many kinds of investigation, require prisms, lenses, and windows ground from some crystalline material having the desired spectral range and other optical properties. The method employed in the growing of such crystals is based principally on the material involved and sometimes the use to which they will be put. In general, it seems that most of the optical requirements can be met by controlled cooling of the fused salt. This method has also proven successful for obtaining crystals of certain semi-conductors such as germanium and silicon.

Four fundamental methods of growing crystals are generally recognized: (a) from the vapor, (b) from solution, (c) from the melt, and (d) growth in the solid.

In this thesis, only the growth from the melt is to be considered.

There are only two recognized ways of causing crystal growth in this manner. Since the action cannot occur simultaneously in all parts of the melt, either a seed crystal must be introduced, or conditions must be such as to favor the formation of spontaneous nuclei. The first method is sometimes employed, an account being given for the growth of potassium bromide crystals (4, p. 322) wherein a water-cooled seed crystal is introduced into the molten salt.

A seed crystal is evidently formed only when out of the random motion of the molecules in the melt, a few fall into the correct pattern. To retain such a seed, it must be cooled below the melting point, i. e., supercooled, and permit other molecules to drift toward their positions. The temperature at which a seed crystal can grow is evidently just lower than that for which

$$(C - L) = D$$

where C is the cohesive forces of the seed crystal, D represents the forces between the crystal face and surrounding liquids, and L represents the disintegration forces (5, p. 372).

Theories on the growth of crystals are not as yet very well developed. Gibbs had stated the thermodynamic requirements in 1865, but to date, there are only qualitative

concepts to help understand the process (6, p. 270). Of interest is the theory of the "embryo" suggested by Frenkel. On the basis of statistical theory, a small group of atoms, less than the critical size of a stable nucleus, can exist at temperatures far in excess of freezing.

In the present experiment, the method first given by Bridgeman (3) and later refined by Stockbarger (10, 11, 12) is considered. The procedure is that of slowly lowering a pointed bottom crucible, containing the growing crystal, through a region of high temperature gradient. Two separate furnaces of slightly differing temperatures are provided, the gradient occurring between these two. The crystal, after being formed, is thus stored in a hot region in order to prevent mechanical strains from forming. A vigorous bombardment of the liquid solid phase boundary assists in the rejection of impurities.

In the actual experiment, a small lithium fluoride crystal was grown. This material was chosen because of its particularly wide spectral range and the fact that it transmits further into the ultra-violet than any other known crystal. It is reported to be one of the most difficult crystals to grow, however. Stockbarger's procedures were extensively used, the principal difference being in the controlling of the temperatures. All

experimental results will be given as a possible guide to others who may wish to continue this work.

All of the alkali halide crystals belong to the cubic system, lithium fluoride, in particular, being a simple cubic.

Fig. 1-a shows the general view of the laboratory space available at Adair Village, where the present work was done.



Fig. 1-a. General view of interior of the building.

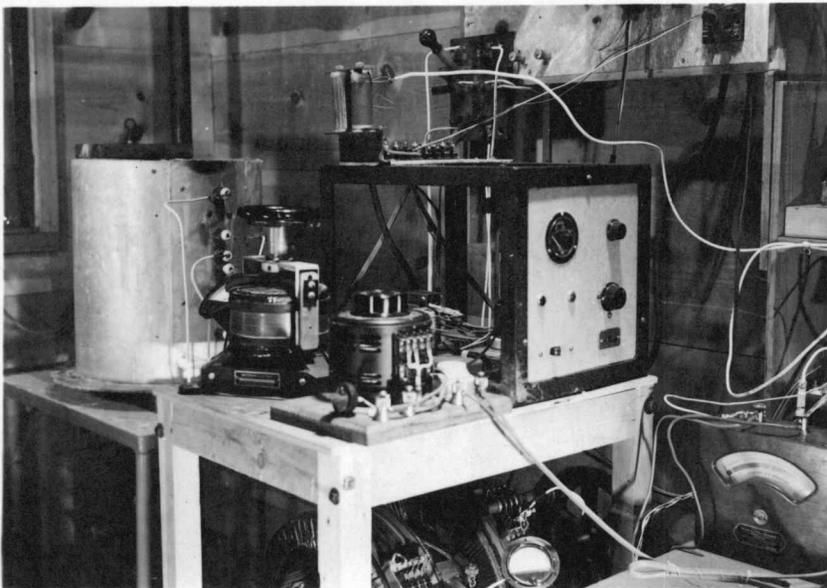


Fig. 1-b. Part of experimental apparatus.

THE FURNACE

Fig. 2 gives a section and plan of the furnace as constructed. The decision to cast the outer walls out of crushed firebrick and high temperature cement was based on the availability of these materials. Removal of the front loose section is readily accomplished with the present design, and access is thereby gained into the inner alundum cores with their windings of resistance wire and linings of sheet stainless steel. The leads from the furnace heating coils are brought out through this removable section, the reason being that any future changes could be made more easily in this than the main part of the furnace.

The windings are of #15 Chromel-A wire, a resistance material suitable for temperatures considerably in excess of those needed. Consideration of several other furnace designs led to the choice of this size of wire. The upper winding is tapped to enable subsectional heating, and it would have been desirable to do likewise with the lower. The purpose is, of course, to make it possible to obtain the best gradient conditions. The outside of the core and windings are covered with a layer of alundum paste.

The cores were lined with 22 gauge stainless steel sheet to give a more even distribution of heat. It is probable that sheet nichrome would resist corrosion better, but at the time this material was not available. Copper

was considered, but it is reasonable to suspect that it would oxidize rather quickly.

The baffle was of aid in achieving the desired gradient. Stockbarger (10, p. 134) reported the use of platinum for this, but on the present project, stainless steel was used and while, no doubt, inferior to platinum, was at least usable. In order to accomodate various sizes of crucibles, the initial construction provided only a protruding ledge to rest the proper baffle on.

The outside radiation shield was rolled from No. 22 gauge sheet iron. A double layer of sheet asbestos was cemented (with sodium silicate) to the interior to allow expansion of the refractory material, this being done before pouring the refractory material. Various other details may be noted in the drawings.

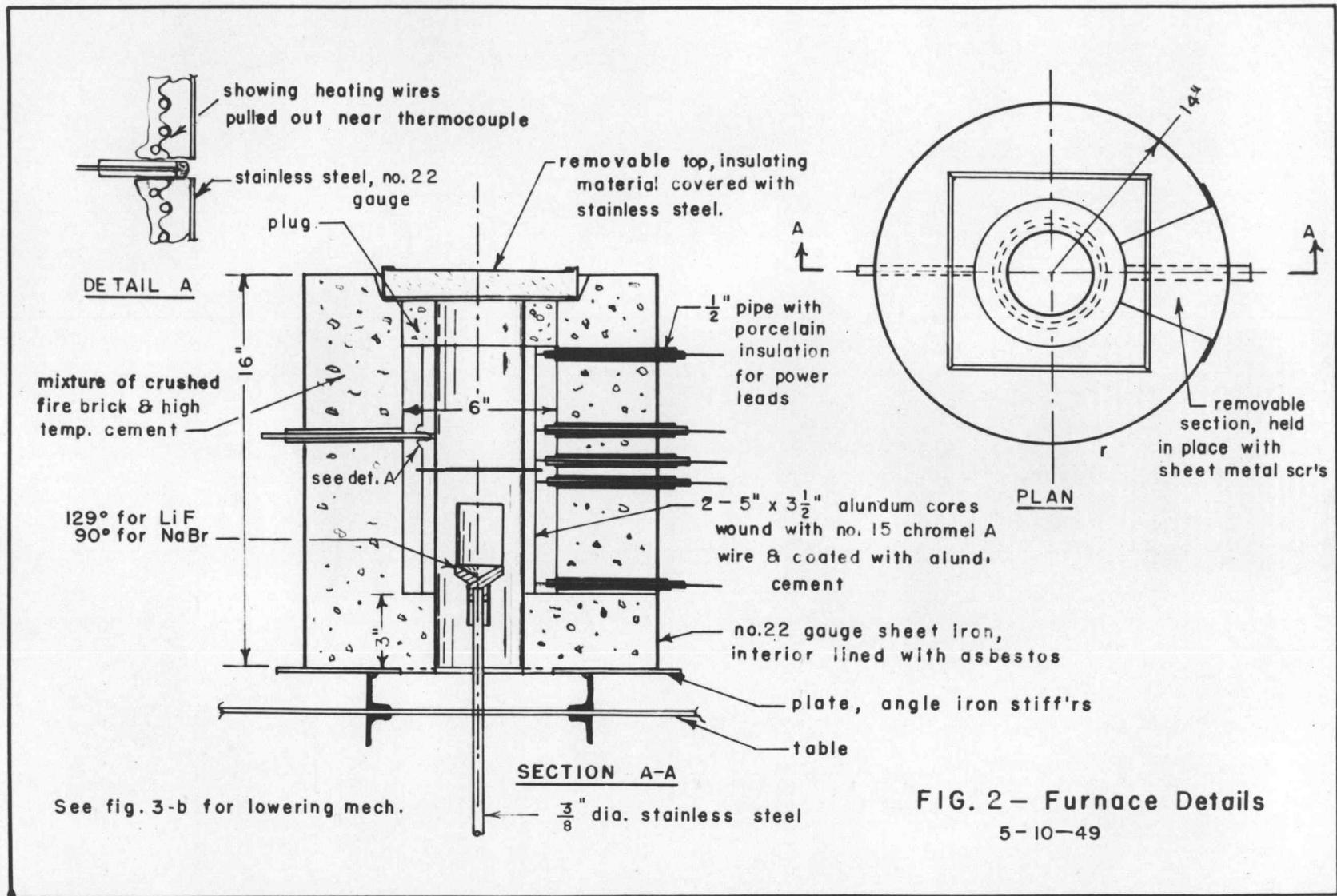
It is certainly possible to construct a furnace with many possible modifications, as for example, having a smaller winding on the inside of the core to act as a rapid temperature correction device (considering the time lag of the main windings).

Notable are the details of the thermocouple. The furnace windings were arched up to clear the fused silica tube containing the leads, the object being to obtain a measure of the interior furnace temperature rather than that of the windings.

For holding the furnace and lowering mechanism a steel frame table with an asbestos board top was constructed. The furnace was cast on a 1/8" steel plate, reinforced with angle iron, and this was bolted to the table.

Bridgeman has indicated that he used a lowering rate of about 4 mm per hour, while Stockbarger, working with lithium fluoride, let the crucible drop only 1 mm per hour. The present arrangement, as given in fig. 3-b, was designed to operate at 2 mm per hour. A 1 r.p.m. synchronous clock motor was arranged to drive a 3/8" diameter brass drum through a system of reduction gears. A small wire cable, unwinding from the drum, allowed the crucible to drop under its own weight. This arrangement seemed to be the easiest to construct and yet give a smooth and steady motion.

The rod and holder which supported the crucible were both made of stainless steel. The design of the holder affects to a limited extent the cooling of the crystal, but not much attention was given to this detail, the shape being as indicated in the drawing. The shielding on the lower side is also of concern in the cooling behavior. It would be well to protect this part with a covering of platinum foil as fairly rapid oxidation was noted.



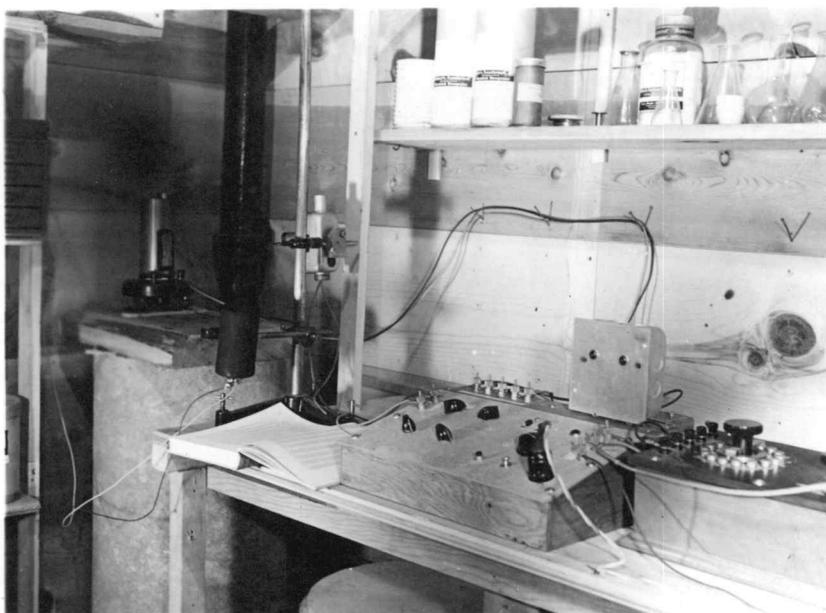


Fig. 3-a. The control apparatus.

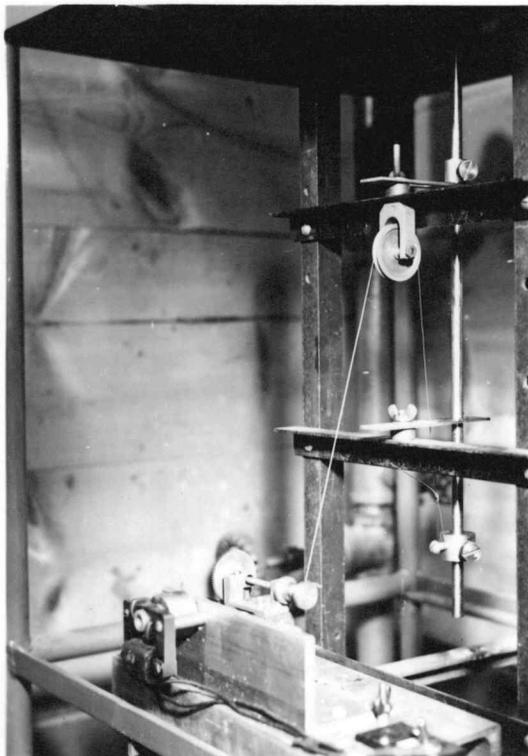


Fig. 3-b. Lowering mechanism.

CRUCIBLES

The greatest single difficulty was found in the production of a suitable container for the melt. The idea of platinum plating a steel crucible seemed practical at first. Several attempts were made to produce a good steel crucible, since the conical bottoms could be readily stamped out with a die, but all attempts at welding of thin sheet iron were discouraging, both from the standpoint of welding without burning holes, and subsequent cleaning to get a surface clean enough for plating. Copper was tried next, its melting point being reasonably above that of lithium fluoride.

Two formulas for electro plating platinum were found (2, p. 313) and are as follows:

	N	g./l.	
"Platinum (as chloride)	0.1	5	12 dwt./gal.
Ammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$	1.0	45	6 oz./gal.
Sodium phosphate $(\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O})$	2.0	240	32 oz./gal.

"In preparing this solution, the three compounds are dissolved separately in water and the ammonium phosphate solution is added to the platinum chloride. This produces a yellow precipitate of ammonium chlorplatinate, $(\text{NH}_4)_2\text{PtCl}_6$. Without filtering this solution the sodium phosphate solution is added, which dissolves the yellow precipitate. The mixture is then boiled for a few hours, or at least till no odor of ammonia can be detected. It is not possible to state just what is the final product in the solution. It appears probable that the platinum is still present in the platinum form (Pt^{IV}), probably as a double or mixed phosphate, or as an "ammino" compound. As the platinum chloride usually contains some free hydrochloric acid (combined to form H_2PtCl_6), and as some ammonia is evolved during the boiling, it appears probable that the final solution contains an appreciable amount of the primary

phosphates such as NaH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$.

"A modification of the phosphate bath is as follows:

	N	g./l.	
Platinum (as chloride)	0.08	4	10 dwt./gal.
Ammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$	1.00	45	6 oz./gal.
Boric acid (H_3BO_3)	0.50	15	2 oz./gal.

"The platinum solutions are operated at a temperature of about 70°C . (158°F .), and with a low-current density, usually less than 0.1 amp./dm.^2 (1 amp./sq.ft.). Difficulty is experienced in securing thick impervious deposits of platinum from this or other solutions. The thin deposits are found to exert very little protection against the action of acids or fumes, owing to the fact that they usually have fine cracks, probably caused by contraction of the platinum during deposition."

Only the first formula was tried. It was necessary to prepare the chloroplatinic acid, as none was found immediately available. This was done by dissolving platinum scrap in aqua regia and boiling with excess hydrochloric acid (l. p. 367) to remove the nitric acid. Platinum dissolves very slowly, and hence, in the event of future interest, it might be advisable to look into the suggestion that it be electrolytically assisted into solution.

The platinum appeared to give a good deposit on the copper when conditions as described in the formula were sustained. However, attempts to melt a sample of lithium fluoride on a surface so prepared, destroyed the platinum coating, in support of the comments in the foregoing quotation. Pre-plating with gold would be a reasonable

suggestion for investigation. Inasmuch as the process of satisfactorily electroplating is concerned with the development of crystals of small size, the problem would probably have to be carried into a detailed study of the whole process (See, for example 8, sec. 20.). It is doubtful, though certainly desirable from the expense standpoint, if a suitable substitute for a regular platinum crucible could be found.

The next attempt was made by fabricating a crucible from 0.0015 in. thick platinum sheet. A form of brass stock was turned out with the exact shape of the crucible and used as an anvil for spot welding. First attempts indicated a tendency for the platinum to weld to the brass, but this was not so troublesome with copper. Not having stock of the required size available, a thick coating of copper was electroplated onto the brass anvil.

The 4.5 cm diameter by 4.5 cm tall cylindrical section was easily made. Both this and the conical bottom were of double thickness of the thin sheet. Stockbarger, in his work, found a smaller danger of leakage through small holes with this laminated construction (9, p. 135). The conical bottom was fashioned by cutting out the sector of a circle and lap welding the edges. An attempt was made to lap weld the edges to the cylindrical portion, but much trouble was found in getting this water tight.

A strip of platinum was welded around the whole area, the entire crucible then being heated to red heat and lightly hammered. After this treatment, no leaks were apparent, but, unfortunately, failure did occur during the preliminary trials with the crucible filled with molten lithium fluoride. It is of great importance that this does not happen since the corrosive action of the salt is disastrous to the lining of the furnace.

For future work, the possibility of welding with a small hydrogen flame or other possible methods should be considered.

The crucible is mounted on its holder by means of alundum cement. This should be allowed to dry before putting in furnace.

CONTROLLING THE TEMPERATURE

Upon the first consideration of the problem of temperature control, it was planned to follow Stockbarger's method. He had used, similar to the present apparatus, a pair of thermojunctions which could cause a condition of unbalance in a galvanometer-potentiometer circuit. A beam of two phase modulated light was projected onto the galvanometer mirror, only that phase being allowed to arrive as determined by the direction of unbalance. An amplifier increased the power level of the photocell output so as to drive a motor whose direction of rotation was phase determined. This motor was, in turn, coupled to four 2 KVA variable transformers. This is only a bare outline and should future interest in this scheme arise, the original article (11) should be consulted.

Lacking suitable transformers to follow the above plan, the next thought was that an increment of the controlling voltage might be handled with a 5 ampere Variac. Considerable time was given to the design and construction of a power transformer to operate in conjunction with such an arrangement. The following empirical formula (12, p. 105), giving the minimum required cross-sectional area in square inches and suitable for small units using silicon steel, was found useful:

$$\sqrt{0.16 \text{ primary volt-amperes}}$$

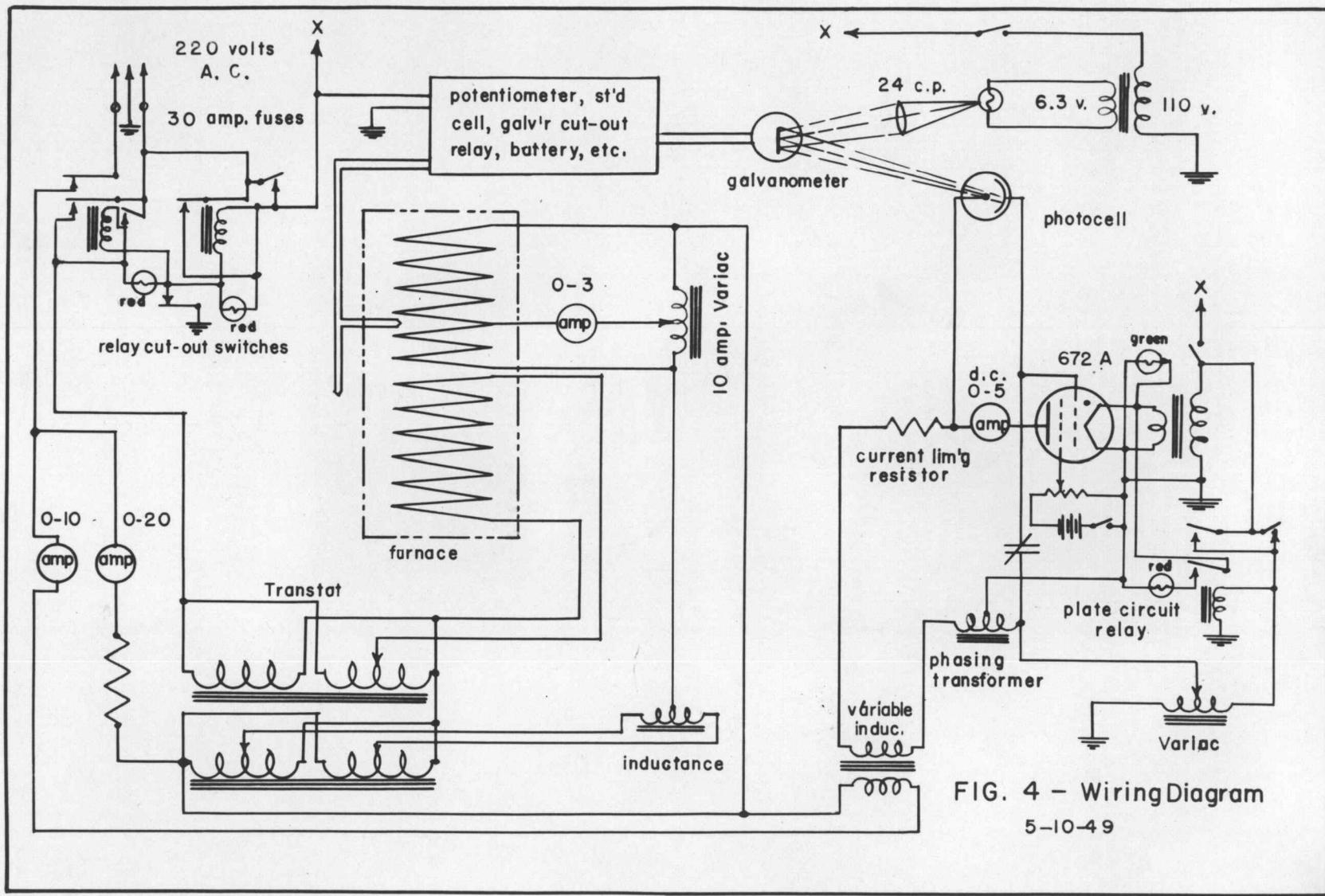


FIG. 4 - Wiring Diagram
5-10-49

Detailed information on transformer design (8, p. 551-553) is, of course, available.

Work on this was discontinued upon securing a 11.5 KVA American Transformer Company Transtat. This is composed of four separate windings on two cores and all connected in parallel for 110 volt operation. As received, all commutator leads were brought out through a tap changing inductance to a common terminal. This was reconnected in the manner illustrated by fig. 4. A reversible motor was then mounted on the Transtat and work was started toward a duplication of Stockbarger's method.

Time limitations, however, imposed the necessity of adopting some shortcuts. A circuit due to Hancock and Zabel (13) was considered, and quickly constructed. This entailed the use of a series resistor in the primary circuit having a voltage drop of about 50 volts. A phase controlled thyatron was arranged to become conducting in the event of falling temperature. The current through the thyatron paralleled that through the series resistor. This scheme was not successful since only a d. c. component was added to the Transtat. For successful operation, two thyatrons should be arranged to pass the entire a. c. cycle.

A saturable core reactor seemed a logical expedient. Having available a 1.5 KVA pole transformer with two

isolated windings, an experiment was run by connecting one winding in parallel with the series resistor and allowing the thyatron to pass a rectified wave into the other. Very promising results were obtained.

The complete wiring diagram is given in fig. 4. The control exerted by the thyatron was well within the time lag limitations set by the furnace. The initial run was made at night and not until about 5:30 A. M. did it become necessary to adjust the Transtat to compensate for line voltage changes, which at this time had begun a steady decrease. The exact degree of control was not determined, but a qualitative approximation based on the sensitivity of the galvanometer circuit indicated a temperature variation of less than 1°C . About 3 hours pre-heating were required to bring the furnace up to a steady state. An appreciable effect was noted upon opening the door to the room, this causing a lowering of the room temperature.

With the adoption of the thyatron control, it was planned to construct a voltage regulating device, perhaps basing the control on an amplification of a sample taken from one of the commutator leads of the Transtat. Two relays could then be used to control the motor.

The thermojunctions were made of No. 22 chromel and alumel wires, being introduced into the furnace through a silica tube. The furnace end was closed with a mixture of

alundum cement and sodium silicate. For the cold junction, a cork lined box was constructed. The junction was mounted in a glass tube, sealed on the lower end and immersed into a small thermos bottle containing crushed ice. The thermos bottle, in turn, was mounted in a metal bucket which was also filled with pieces of ice. It was found that ice remained in the thermos bottle for more than 36 hours without additions to the outer container, the room temperature averaging about 20°C.

The galvanometer used had a sensitivity of, roughly, 3×10^{-9} amperes per mm of deflection and a resistance of 18 ohms. The mirror was illuminated by a 24 c.p. auto lamp mounted in an outlet box and equipped with a suitable lens system.

Some effort was directed toward the construction of a potentiometer, the available literature (8) being consulted. For the initial experiment, however, a Leeds and Northrup student type instrument was used. The switching circuit, used for preliminary balancing and checking with a standard cell, was made up into a unit and under the control of a relay. In the event of a power failure, the master relay would open and in this manner the galvanometer would be automatically cut out of the circuit. Thought has been given to extending this relay protection to a possible failure of the hot thermojunction, but no satisfactory idea has come forth.

A Western Electric 672A tetrode type of thyratron was used for this experiment. The 672A has an average rating of 3.2 amperes and, by virtue of the screen grid, has a variable control characteristic. This latter fact made the tube more useful in adapting it to the other components as were available. Five minutes must be allowed for the heating of the filament before the load is imposed on this tube.

A gas type photocell was used, and this, together with a variable capacitor, comprised a phase shift circuit. A triangular slit was placed in front of the photocell so that the degree of illumination would depend on the relative deflection of the galvanometer. The principle of phase shift control of a thyratron is well covered in the literature (7, p. 190-191). Fig. 1-b shows the thyratron unit as mounted above the Transtat.

It is important that the freezing level be determined and the current increased so as to hold this point consistently constant, since it is subject to variation as the crucible is lowered. For the present experiment, the current as measured by the ammeter in the lower section of the top winding was noted for the initial and final positions of the crucible, this current being sufficient to just maintain the molten state. One could certainly expect this to be an unsatisfactory approximation, and some study should

be given to a better way of determining the freezing level. One method might be worked out whereby an auxilliary thermocouple is placed at a point just above the baffle, and a periodic observation made. Stockbarger (11, p. 417; 12, p. 210) gave some details on this but it would be advisable to communicate with him for more complete details. He indicated that his potentiometer was caused to change slowly by a motor drive.

PREPARATION OF PURE LITHIUM FLUORIDE

In the preparation of pure lithium fluoride, Stockbarger's outline was followed. Only a brief account of the process need be given here as this paper (10, p. 135) is easily obtained.

The purest possible lithium carbonate (Merck, reagent grade was used in this experiment.) is converted to the bicarbonate by bubbling in carbon dioxide under pressure. Fig. 5-a illustrates the method used for the preliminary trials, a column of water being the pressure determining device. For future work, a bomb has been built, however. Because the bicarbonate is more soluble than the carbonate, calculations should be based on a saturated solution of the former. After allowing suspended material to settle and after double filtration, the clear liquid was mixed with a slight excess of hydrofluoric acid and allowed again to settle. All this work was carried on in carefully cleaned bottles, the mixing with the acid taking place in a paraffin lined wooden vat of about 5 gallons capacity. Care should be taken with such a vat as troublesome, but not serious leaks were encountered. Perhaps, first lining the vat with one of the available roofing compounds would help relieve thermal stresses set up in the paraffin.

The liquid in the vat was then removed, leaving a good precipitate. This was transferred to sheets of wax

paper and slowly dried in an oven. The purity of the salt was quickly checked by the sintering test, the desired indications being a definite melting point, a translucent and partially transparent button. This was all as it should be.

The crucible was loaded in several steps, since time must be allowed for the salt to fuse and contract. Stockbarger mentions an alternate method of pre-sintering to make but one loading necessary. Precautions against side and top heating are to be noted. Finally, the platinum top is put on the crucible.

The results of the chemical calculations were as follows:

Crucible volume, about	78.5	cc
Specific gravity of LiF.....	2.295	
Amount LiF required	235.5	gr
Molecular weight of LiF.....	25.94	
Amount of Lithium required.....	63.	gr
Li ₂ CO ₃ required to supply required lithium	332.	gr
LiHCO ₃ that should result	617.	gr
Solubility of LiHCO ₃ at 13°C	5.5	gr/100 cc
Water required, about	11.	liters



Fig. 5-a. Treating lithium carbonate.

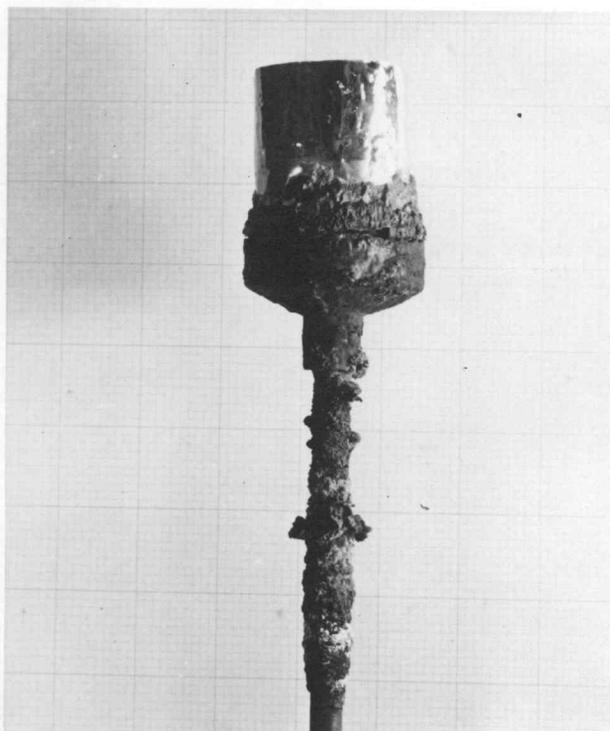


Fig. 5-b. Crucible at
end of trial
run.

PRELIMINARY RESULTS AND COMMENTS ON FUTURE WORK

While it has been indicated that the crucible failed in the initial trial, enough salt remained to permit the growth of a single crystal of a few millimeters thickness. A second trial is being contemplated at the writing of this thesis where attention will be directed toward the solution of the two main problems so far encountered. These are (a) making leak-proof crucibles, and (b) methods of determining changes in the freezing level as the crucible is lowered.

Another problem which seems evident at this time is the removal of the completed crystal without injuring the crucible. A suggestion has been given for the case of sodium bromide (10, p. 417) whereby the crystal is inverted in the furnace and the temperature raised to the melting point. Suitably designed tongs are counterbalanced on a pulley system so as to lift the crucible and leave the crystal behind.

Considering the high market value of single lithium fluoride crystals, and in view of their utility, it seems that any future work is fully justified. In addition to the wide spectral range of lithium fluoride, its very low dispersion in the visible region of the spectrum (the index of refraction ranging only from 1.3906 at $6563\overset{\circ}{\text{A}}$ to 1.397 at $4358\overset{\circ}{\text{A}}$) makes this a most desirable material.

The cutting and grinding of these crystals should present no great problem. A copper blade charged with water and carborundum seems to be sufficient (10, p. 136).

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