MASTER

THE PRODUCTION OF LiF SINGLE CRYSTALS WITH

SELECTED ISOTOPIC RATIOS OF LITHIUM

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OAK RIDGE NATIONAL LABORATORY
operated by
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U.S. ATOMIC ENERGY COMMISSION

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ISOTOPIC RATIOS OF LITHIUM

C. F. Weaver, R. G. Ross, B. J. Sturm,.
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ABSTRACT

The purpose of this research was to develop the techniques
and apparatus necessary to produce single crystals of LiF with
selected ratios of the lithium isotopes containing not more than
a few parts per million impurities. The starting material was
prepared from purified aqueous solutions of LiOH and HF and was
dehydrated in the molten state with anhydrous HF. The dehydrated
LiF was then converted into a single crystal in a unique Stockbarger
furnace which has a window allowing visual monitoring of the crys-
tal growth and variable electrical shunts making possible the
application or removal of thermal gradients at will. Crystals
weighing several hundred grams and containing 99.99, 98.06, and
96.50 at. % lithium-7 have been produced as part of a sequence
which will include 87.60, 79.28, 69.24, 50.77, and 0.7 at. %
lithium-7. These crystals do not display strain under polarized
light and do not show OH⁻ absorption of infrared radiation. The
purest crystals produced contain less than 1 ppm cationic impur-
ities according to the results of emission spectroscopy and
neutron activation analysis.

INTRODUCTION

Research programs within the U. S. Atomic Energy Commission frequently
require special materials which are unavailable from commercial suppliers.
Some of the demand for such items is met by a Pure Materials Program at
ORNL, to which several Laboratory divisions contribute and which is coordi-
nated by the staff of the Solid State Division of the Laboratory. High-
purity single crystals of LiF with selected isotopic ratios of the lithium
isotopes are among the materials in demand.

Lithium fluoride possesses physical properties which have long produced
great interest in single crystals of this material. It transmits further
in the ultraviolet region than any other known solid material.[1-7] Its

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*Present address: Kawecki Chemical Company, Boyertown, Pennsylvania.

dispersion in the visible spectrum is low.[1,8,9] In the infrared region from 2 to 5µ, of special use for analysis of organics, it has a higher dispersion power than either NaCl or CaF_2.[10] These properties and the cubic symmetry, stability in air,[2] hardness,[4-11] (except for ultrapure material[7]) and resistance to discoloration with use[4] make the material of great value in ultraviolet and infrared spectroscopy.[3] It can be used in conjunction with quartz to make achromatic and apochromatic lenses for ultraviolet use.[3,6,8,9] Its high transmission in the vacuum ultraviolet range makes it suitable for use in Cerenkov Counters.[7] It was used in an ultraviolet telescope in Ranger space vehicles.[7] Lithium fluoride can be grown from the melt in unusually perfect condition, can be cleaved with negligible distortion, and is easily etched. These properties allow studies of dislocation origin, movement, and multiplication.[12,13] Many of the physical properties of LiF such as thermal conductivity,[14] refractive index,[15] infrared absorption and reflection,[16] unit cell size,[17] and neutron absorption cross section depend on isotopic content. Neutron irradiation studies on LiF with natural isotopic abundance are complicated by the generation of H_2,[18] He,[18] F_2,[19,20] and colloidal Li.[19-21] Thus it is desirable to produce single crystals of LiF with selected isotopic ratios.

HISTORY OF GROWTH TECHNIQUES

Several techniques have been described in the literature for growing LiF crystals. Melts have been frozen from both top[11,22] and bottom.[23] In both methods the freezing-point isotherm is moved through a stationary melt. Two disadvantages of these methods are that, with large samples or high thermal gradients, the melt becomes hot enough to volatilize and the crystal may crack under thermal stress.[1,23] The technique generally used today[1-3,6,24,25] involves moving an LiF melt and its container through a furnace within which the isotherms remain essentially stationary. This procedure has the advantage of allowing temperature gradients which are large near the liquid-solid interface and small elsewhere. Thus the melt is not overheated and the solid ingot may be annealed under a small thermal gradient. This procedure, devised by Bridgman for metals,[26] was modified by

Stockbarger[1,24,25] for application to ionic crystals. Stober,[27] Ramsperger and Melvin,[23] and Strong[28] described the general conditions which must be met to yield large flawless crystals, and these are satisfied by the Stockbarger furnace. Briefly, these conditions are:

1. The crystallization must start at a single point at the bottom of the capsule.[27,28] This point must have the lowest temperature to avoid the formation of other crystals.[23]

2. There must be a large vertical temperature gradient at the liquid-solid interface[27,28] in order to enhance the rejection of impurities[1,24] and minimize the movement of the isotherms.

3. Isothermal surfaces within the capsule must be nearly horizontal to prevent convection currents in the molten salt.[23,27,28]

4. The melting temperature isotherm must be moved through the melt slowly and uniformly so that the crystal formed at this surface will be flawless.[27,28]

5. After the crystal has been formed and while it is still plastic, the bottom and top of the crystal must be brought to the same temperature to prevent strains introduced by unequal contractions at room temperature.[23,28]

6. The crystal, once formed, must be cooled very slowly to room temperature to avoid thermal stress which increases dislocation densities.[12,23]

One of the specific conditions emphasized in the earlier literature for producing single crystals of LiF is the requirement of an inert atmosphere. As early as 1926 Slater[11] reported difficulty in growing LiF crystals in air. Schneider,[5] and later Stockbarger,[25] recommended the use of vacuum to avoid chemical reactions with air. Vasilyeva[2] recommended the use of vacuum not only to avoid reactions with atmosphere but also to allow the escape of volatile impurities. Both Stockbarger and Vasilyeva

used furnaces capable of operating at a fraction of a micron pressure. More recently Feuerstein and Parker[29] reported growth of lithium fluoride crystals under 25μ pressure. Eckstein et al.[30] have confirmed Vasilyeva's claim that many impurities will evaporate easily from molten LiF in vacuum.

It has been reported that Pt,[1,2,5,6,11,23,25] Fe,[2] Ni,[2] Mo,[2] W,[2] Ta,[2] and graphite[2,25,29] do not react with LiF if suitable atmospheres are used. Pt and Ta, however, stick to the LiF ingot. If these metals are used as containers, the LiF will be strained during cooling unless very thin walled capsules,[1,23,24] which will collapse as the crystal shrinks, are employed or the sample is removed from the container at high temperature.[6,25,28] Of the remaining materials, the ease of fabrication, strength at high temperatures, and inertness to an H_2-HF-molten LiF environment make Ni the optimum choice as the container material.

Crystal growth rates from 0.1 to 1.5 mm/hr,[1,23,25,29] thermal gradients at the solid-liquid interface from 5 to 10°C/cm,[28] temperature control to less than ± 1°C,[8,28,31] cooling periods up to 240 hr,[6,23,28,29,32] and cone angles of 120 to 130°[1,3,29] have been recommended. These conditions were generally met with the exception that a cone angle of 60° was used in order that a smaller number of seed crystals would be formed, thus facilitating the formation of a single crystal.

MATERIALS PREPARATION

Unusually pure materials were needed for the starting charge[1,2,24,25] since several regrowths to eliminate impurities are time consuming, and ions such as Mg^{2+} which fit in the LiF lattice[33-35] might not be removed at all. Several methods are listed in the literature for preparing highly purified LiF.[5,6,24,30,36,37] These were not used since the starting material was high-purity LiOH·H_2O (Table 1), available from the Isotopes Division of this Laboratory. The LiOH·H_2O was further purified by the following procedure, which is based on reports of Apple[38] and Mills and Whetsel.[39] The LiOH·H_2O was dissolved in water which had been distilled from a tin-lined still, deionized with a mixed bed deionizer, and then redistilled from quartz vessels. Polyethylene was used to contain the aqueous solutions.

Table 1. Spectrographic Analysis[a] of Material Used for LiF Crystals

Material	Element (ppm)								
	Al	Ca	Cu	Hg	K	Mg	Mn	Na	Si
LiOH·H₂O		200		100	150	<200		200	
Heat-lamp dried LiF		40	<5	100				5	<100
HF dehydrated LiF	20	100				10	10	<50	

[a]Analysis by J. A. Norris' group, Analytical Chemistry Division, ORNL.

Polyvalent cationic impurities were removed from the solution by extraction of their perfluoro-octanoic acid complexes with diethyl ether. Addition of the purified aqueous solution to an excess of aqueous HF caused the precipitation, in an acid environment, of LiF, which was filtered using a polyethylene Büchner funnel and acid-resistant filter paper. The aqueous HF was prepared by dissolving gaseous HF in the purified water mentioned previously. The anhydrous HF used for this purpose was purified by allowing a portion to escape from the tank at room temperature. Impurities containing silicon and sulfur selectively escaped from the liquid HF. Approximately 1 hr of free flow from a 100-lb tank was found to be sufficient for this purpose. The direct use of HF gas to precipitate LiF was discarded because excess heat (enough to discolor the plastic containers) was generated, and precipitation occurred in alkaline rather than in the recommended acid solution.[1,25] The LiF was then dried in air with heat lamps. Contamination by air-borne particles was minimized at first by preventing smoking in the area,[25,40] covering all solutions, and drying under a plastic tent. Later, the LiF preparation was performed in a plastic clean box with a filtered atmosphere. The air-dried LiF powder was loaded into an H₂ fired, grade-A nickel container. The system was flushed with purified H₂ and heated to approximately 900°C. The molten LiF was then treated with an anhydrous HF + H₂ mixture using an H₂ to HF ratio of approximately 5 to remove any oxides, hydroxides, or moisture which might be present. This method afforded real advantages over the earlier procedure which was to flush the system with purified He and melt the LiF under this He atmosphere. Under these conditions, the moisture present in the air-dried charge caused a small amount

of corrosion which added the constituents of grade-A nickel[41] (nickel, copper, iron, manganese, silicon, carbon, and sulfur) to the melt. With the addition of the HF + H_2 mixture, most of these impurities were reduced and precipitated as fine particles which settled out of the melt. An additional portion of these impurities was segregated by the freezing process forming a brownish central core of the ingot. The portion which was colorless and free of specks was separated from the bulk by hand picking in a vacuum dry box. The yield of usable material produced by this method was approximately 65%. The substitution of H_2 for He reduced considerably the amount of corrosion by inhibiting such reactions as $2HF + Ni \rightarrow NiF_2 + H_2$ which occur even before the addition of HF for dehydration purposes because some of the moisture present in the LiF reacts to form HF ($H_2O + LiF \rightarrow LiOH + HF$). The presence of HF at temperatures below the maximum temperature ($\sim 900^\circ C$) of the process is undesirable since the magnitudes of the free-energy changes favoring the corrosion reactions increase with a decreasing temperature.[42] The yield of usable lithium fluoride was increased to about 90%. Both methods produced material of about the same purity. A typical analysis is shown in Table 1. The principal advantages of the use of an H_2 atmosphere are a smaller loss of product and a considerable reduction in the time consumed in hand picking.

The dehydrated LiF was removed from the nickel pot in a vacuum dry box and stored in a polyethylene container. The He atmosphere in the box was continuously circulated through an activated-charcoal trap, cooled to liquid-nitrogen temperature. The moisture content during this operation was ~ 10 ppm as determined by continuous monitoring of the atmosphere with a Model W Electrolytic Water Analyzer (Manufacturers Engineering and Equipment Corporation, Hatboro, Pennsylvania). Kato[43] has shown that hydrolysis occurs on LiF surfaces in contact with air slightly above room temperature. Patterson and Vaughan[44] have found a gradual decrease in the ultraviolet transmission below 1600 A unless LiF is stored in vacuum or in dry gas. Thus protection of the dehydrated LiF is desirable even at room temperature. At this stage all material which is not completely transparent or colorless was eliminated from the charge. Transparency and lack of color is considered[2,4,17,29,30] to be an excellent test of LiF purity (Table 1). The hand-picked charge was loaded into an H_2 fired capsule which was then sealed, inserted into the Stockbarger furnace, and evacuated to 10^{-3} to 10^{-4} mm.

CRYSTAL GROWTH APPARATUS

The crystal growth apparatus shown in Figs. 1 and 2 is a unique Stockbarger furnace which has a window allowing visual monitoring of the crystal growth and variable electrical shunts making possible the application and removal of thermal gradients at will. The heat source is a Marshall furnace (manufactured by Marshall Products Company, Columbus, Ohio) which has the advantages of being rugged, having high heat capacity useful to suppress temperature fluctuations,[9] and allowing the application and removal of thermal gradients. To enhance the gradient at the melting-point isotherm, a baffle consisting of 1 3/4-in. insulation brick and a silver reflector is incorporated into the nickel liner of the furnace. This combination allows the generation of thermal gradients in the 800 to 900°C range of 0 to 12°C/cm. The gradient may be changed at any time by simply altering the variable resistance shunts shown in the left center of Fig. 2. The rack of equipment to the far left of this figure contains controllers and recorders. The temperature controller in the middle of this rack is a series 60 Leeds and Northrup controller and will control the furnace temperature to ± 0.1°C. The recorder immediately above this controller is a Minneapolis-Honeywell 16 point recorder which continuously monitors the thermal gradients within the furnace. The controller at the top of the rack is a Wheelco Model 401 controller and functions only if the precise controller fails. This decreases the possibility of an extreme temperature excursion. Since the growth-annealing cycle requires about 3 weeks, during which the equipment is generally unattended, such protection is considered advisable. The Leeds and Northrup type K-3 Universal Potentiometer, between the shunt box and the furnace, makes possible the detection of temperature fluctuations which are too small to observe on the recorders at the far left. The liner in the furnace serves the functions of supporting the capsule and baffle, guiding the capsule movement, and containing the He atmosphere which protects the capsule itself. Oxidation is not completely prevented because of air leakage (see Fig. 1) at the baffle, drive entry, and capsule entry. It is, however, reduced to tolerable levels. To the right in Fig. 2 is an oil diffusion pump which is connected to the capsule by a 2-in.-ID stainless steel flexible tube (manufactured by the American Hose Division of the American Brass Company, Waterbury, Connecticut)

QUARTZ WINDOW

2-in. GATE VALVE

TO VACUUM HEADER

DISCHARGE VACUUM GAGE

TO VACUUM HEADER

TEFLON PACKING

VACUUM PRESSURE REGULATOR

HELIUM BLANKET VENT

COOLING H_2O

NICKEL FURNACE LINER

HYDROGEN SUPPLY

0.010-in. SILVER REFLECTOR

HELIUM SUPPLY

$1^3/_4$-in. INSULATION BRICK

THERMOCOUPLE WELL

NICKEL CRUCIBLE

ACTIVATED CHARCOAL COLD TRAP

TWIST LOCK CONNECTOR

MARSHALL FURNACE

THERMOCOUPLE WELL

HELIUM BLANKET IN

TEFLON PACKING

COOLING H_2O
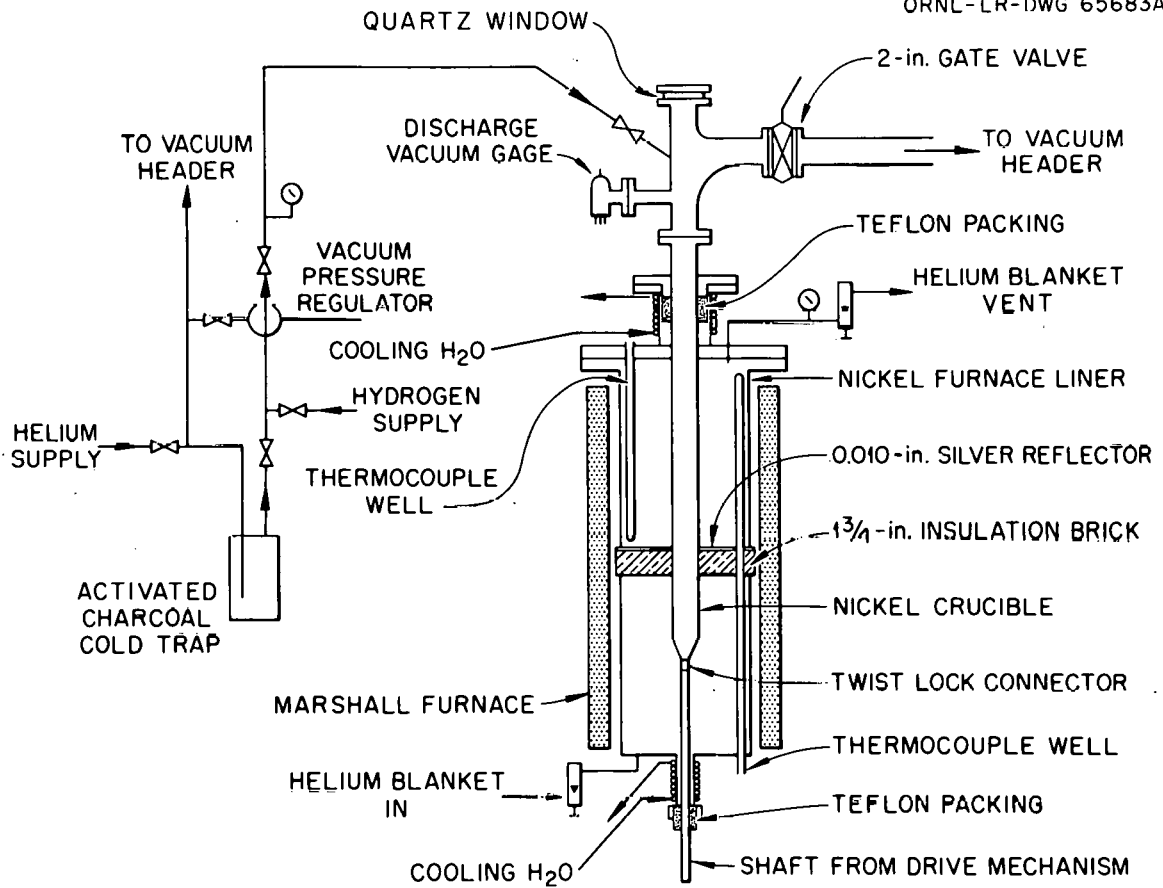
SHAFT FROM DRIVE MECHANISM
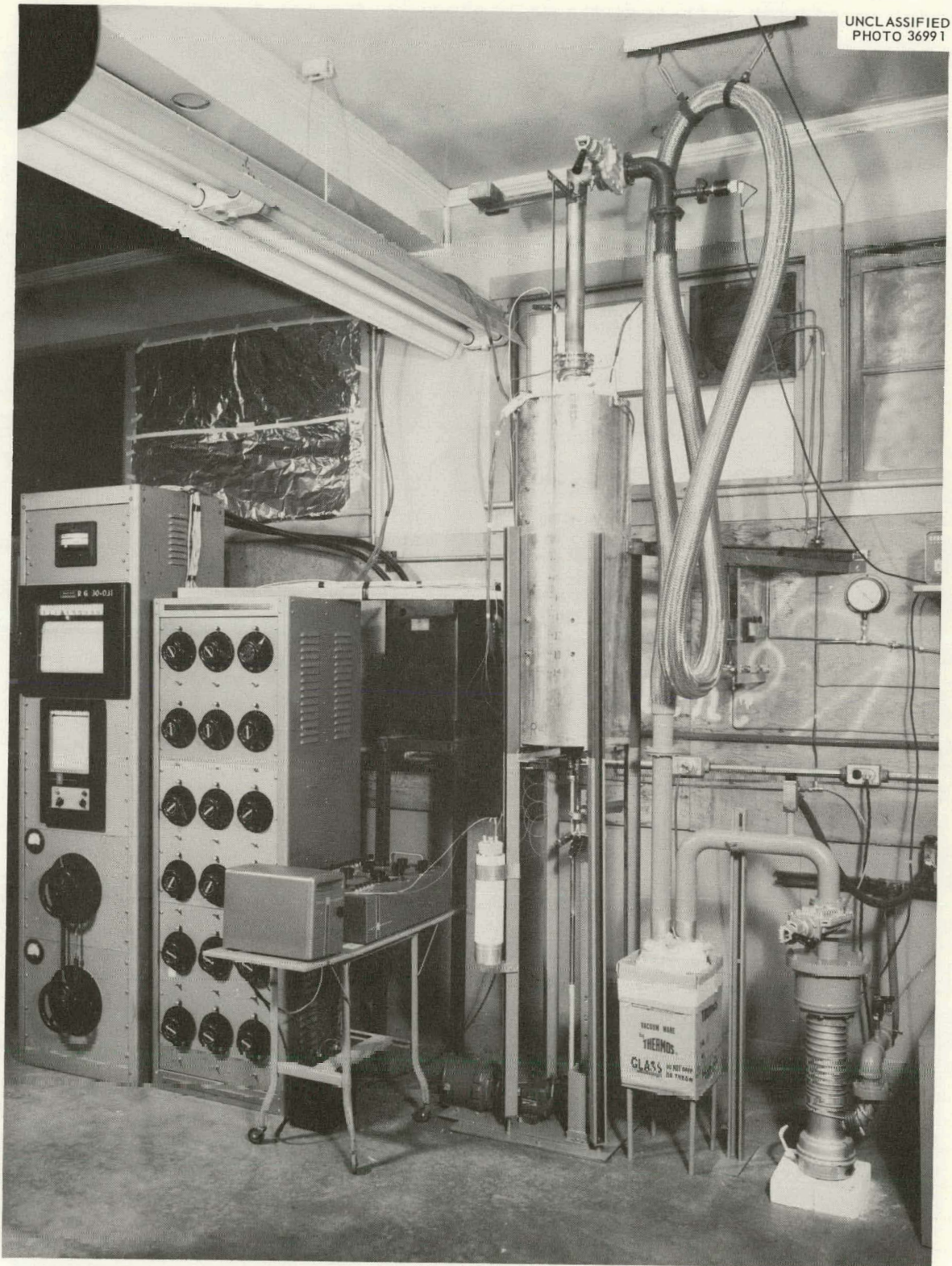
Fig. 1. Stockbarger-Bridgman Apparatus (Schematic).

Fig. 2. Stockbarger-Bridgman Apparatus.

which provides a path from the LiF charge to the inlet of the diffusion pump completely free of constrictions. The pressure obtained in the capsule at the ion gage shown in Fig. 1 is in the 10^{-3} to 10^{-4} mm range. The capsule which contains the LiF charge can be seen extending from the top of the furnace in Fig. 2 and schematically in Fig. 1. The capsule in Fig. 2 represents an earlier version while that in Figs. 1 and 3 is the model in current use. The capsule length was selected to allow the molten lithium fluoride to exist in the bottom while the top (flange region) remained at low temperature. Thus all flanges were relatively cool, allowing the use of O-ring seals. The absence of constrictions inside the capsule, a necessary condition in a highly evacuated system,[45] allows the removal of the lithium fluoride crystal without destruction of the capsule. The portion of the capsule which is in actual contact with the melt has a slightly smaller inside diameter to further aid in the removal of the crystals.

The twist lock connector (Figs. 3 and A5) was so designed that, except for the pin, only compressive and tensile forces were exerted on it. Earlier versions which developed shear stress failed after one or two runs.

A quartz window is included in the capsule header (Figs. 3 and 4), allowing direct observation of the melt during high-temperature operations. Distillation of the LiF sample, bubble formation, and interfaces in polycrystalline ingots were observed through this window. Corrective action may thus be taken without cooling and opening the capsule. Completion of growth was easily observed, and the annealing period started immediately thereafter. This visual as well as thermal monitoring of the growth procedure allowed a great saving of time. There has been no frosting or other difficulties with the quartz window.

The drive mechanism consists of a variable-speed unit and a direct-drive constant-speed unit. The first unit has the advantage of a very wide continuous range of capsule movement rates (from a fraction of a millimeter per hour to 10 cm/hr) but has the disadvantage of erratic motion in the 0.5 mm/hr range. It consists of a 1725-rpm, 1/6-hp, synchronous motor which drives a 10E400R Zero-max variable-speed unit. This output drives a gear train which is directly linked to the capsule. The direct-drive unit operates at only one rate (0.5 mm/hr) but is steady. It consists of a Boston Gear Ratiomotor Model MW121-2400-CT and drives the same gear train which is connected to the Zero-max.
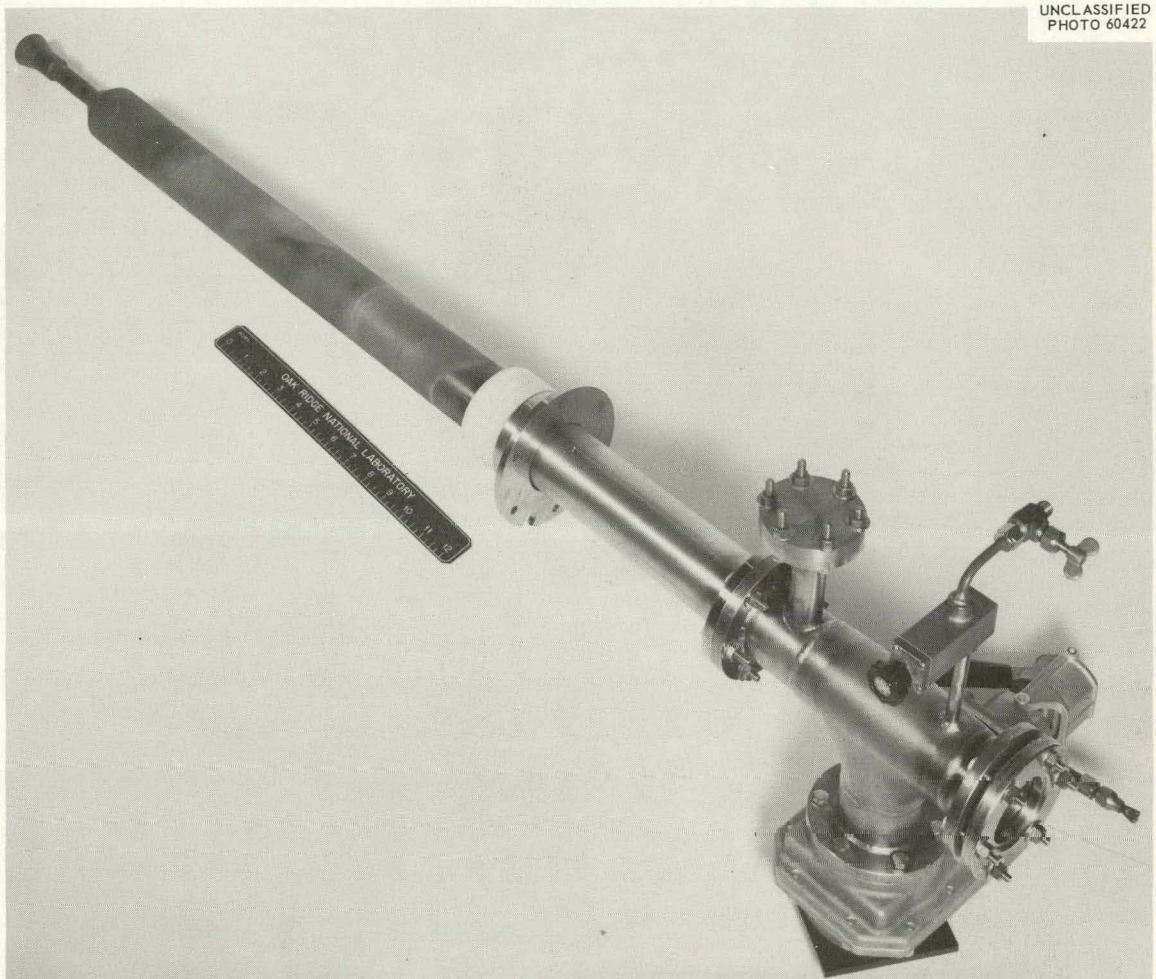
11

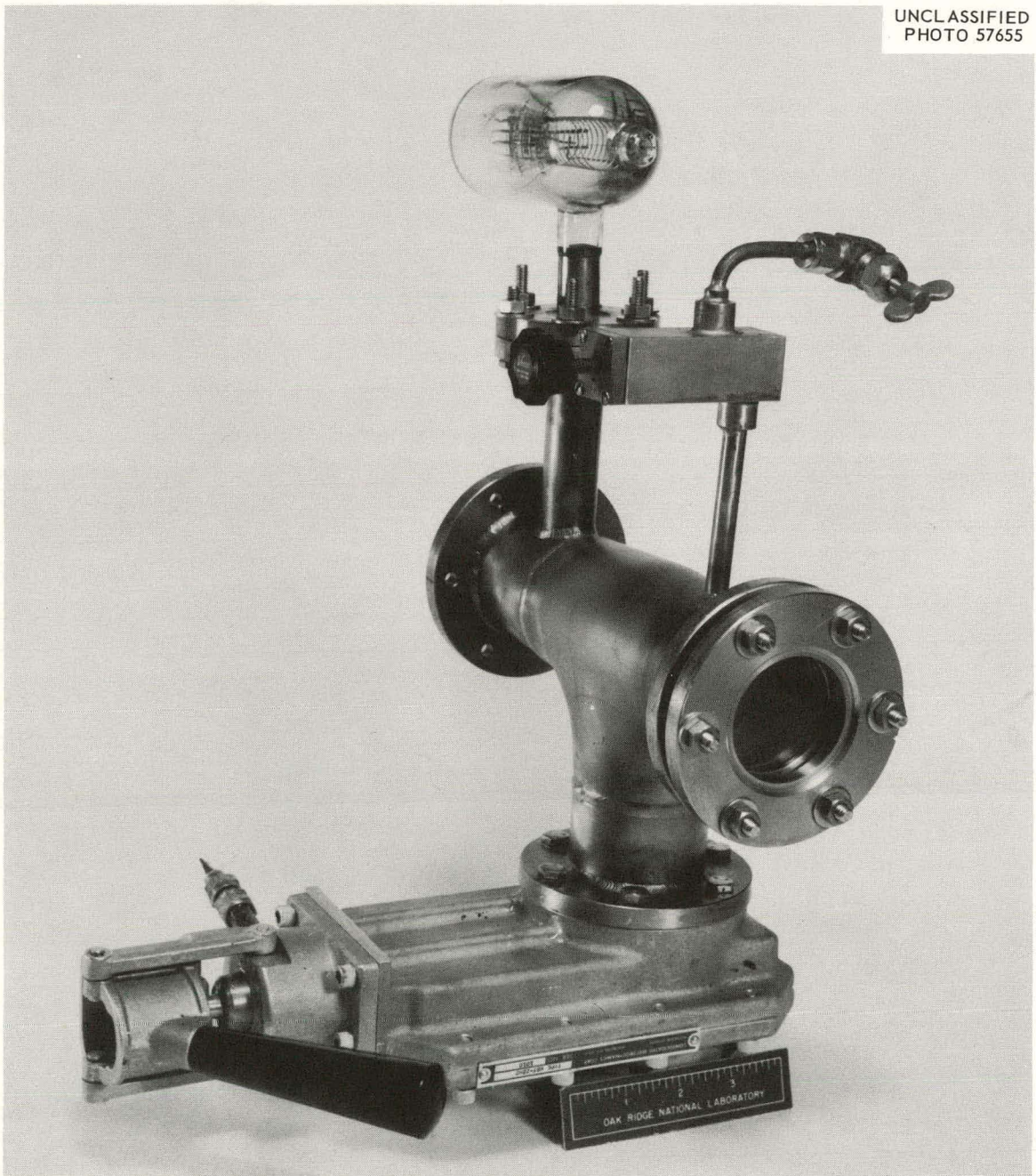Fig. 3.   LiF Growth Capsule with Header and Window Attached.

Fig. 4.   Growth Capsule Header with Window Attached.

Detailed drawings of this apparatus are shown in the appendix (Figs. A1 through A8).

RESULTS AND DISCUSSION

Apparatus and techniques were developed for production of large (300 to 400 g) LiF single crystals of selected isotopic concentration with no more than a few parts per million impurities. Three crystals, containing 99.99, 98.06, and 96.50% Li-7 respectively, have been produced. It is anticipated that crystals containing 87.60, 79.28, 69.24, 50.77, and 0.7% Li-7 will be grown.

It was found that visual as well as thermal monitoring is necessary for the growth of flawless crystals, and that close attention must be paid to the pressure-thermal cycle to allow outgassing while avoiding excessive distillation and bubble formation. To explain the necessity for such requirements, a chronological description of the growth experiments is given below.

In the first attempt to produce a crystal, pressures in the range of 10^{-3} to 10^{-4} mm were employed throughout the entire procedure. The melt was totally distilled and formed a polycrystalline mass near the top of the capsule. This charge was recovered quantitatively after opening the capsule, indicating that little if any of the LiF was distilled past the top. Since no window was present at this time, the difficulty was not detected until after the run was completed, and hence the rate of distillation was not known.

In order to obtain an estimate of the distillation rate under crystal growth conditions, several experiments were conducted in closed nickel containers. It was ascertained that total distillation of liquid LiF occurred in approximately 16 hr at mechanical pump pressure (100 μ), but only a trace of LiF distilled over a 10-day period if 1 atm of He was used. While conducting these distillation studies, it was found that small single crystals of LiF displaying very well formed 100 faces could be grown from the gas phase. These crystals are shown in place in Fig. 5, and a selected crystal may be seen in Fig. 6. Typical conditions for their growth were:

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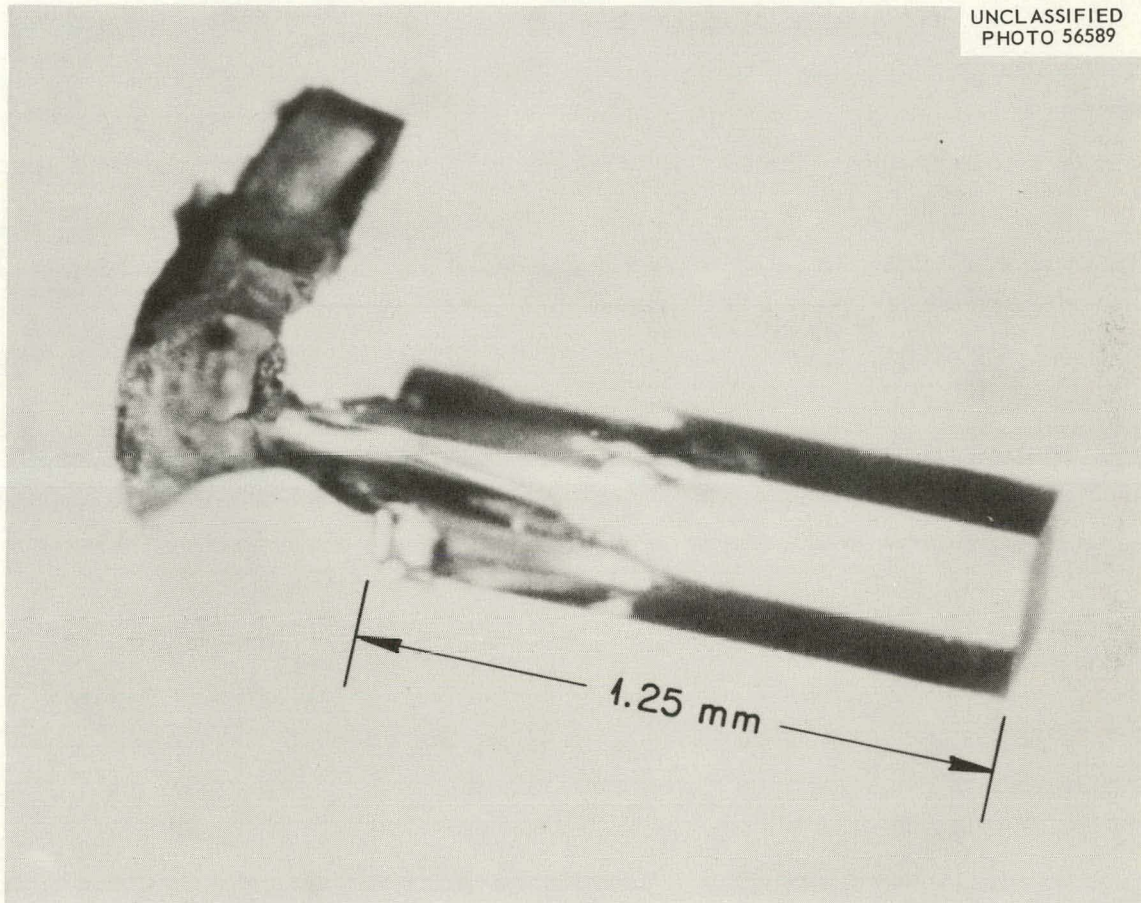Fig. 5. LiF Crystals Grown from Vapor (in Place).

Fig. 6. LiF Crystal Grown from Vapor (Showing 100 Planes).

(1) LiF temperature: 900°C

(2) He pressure: 1 to 1.5 atm

(3) Time: 2 to 4 weeks

The LiF needles were found on the nickel surfaces which were at temperatures slightly less than the LiF melting point (848°C). Surfaces with temperatures much below the LiF melting point or pressures much less than 1 atm produced a polycrystalline mass of LiF with particle sizes in the 1 to 100 μ range.

In the second attempt to produce an LiF crystal from the melt, the charge was outgassed at 10^{-3} to 10^{-4} mm only at room temperature. A positive pressure (1 to 1.5 atm He) was maintained within the capsule during the entire thermal cycle. A usable ingot (Fig. 7) was produced under these conditions, but it consisted of two crystals. Again this failure to produce only a single crystal was undetected until the entire procedure was terminated.

Both failures to produce a large single crystal were related to an inability to observe the charge during the experiment. Therefore, the vacuum-gas header was modified to include a quartz window as shown in Figs. 3 and 4.

The third attempt to produce a crystal involved outgassing at 10^{-3} to 10^{-4} mm both at room temperature and through the thermal cycle until distillation was observed. This procedure tested both the window and time-pressure requirements to avoid a troublesome amount of distillation. Figure 8 is a photograph, taken through the quartz window, of the partly sublimed LiF charge at 830°C. The entire charge was remelted under 1 to 1.5 atm of He and grown into a single crystal and again photographed (Fig. 9) at 830°C. Helium bubbles appear as dark spots in the photograph, and surface markings on the nickel crucible show up as lines. The LiF is transparent under these conditions. After removal (Fig. 10) it was found that the He bubbles were entirely on the surface. This experiment showed that:

1. The LiF could be melted under 10^{-3} to 10^{-4} mm pressure and kept in a molten state for an hour or two without significant loss by distillation.
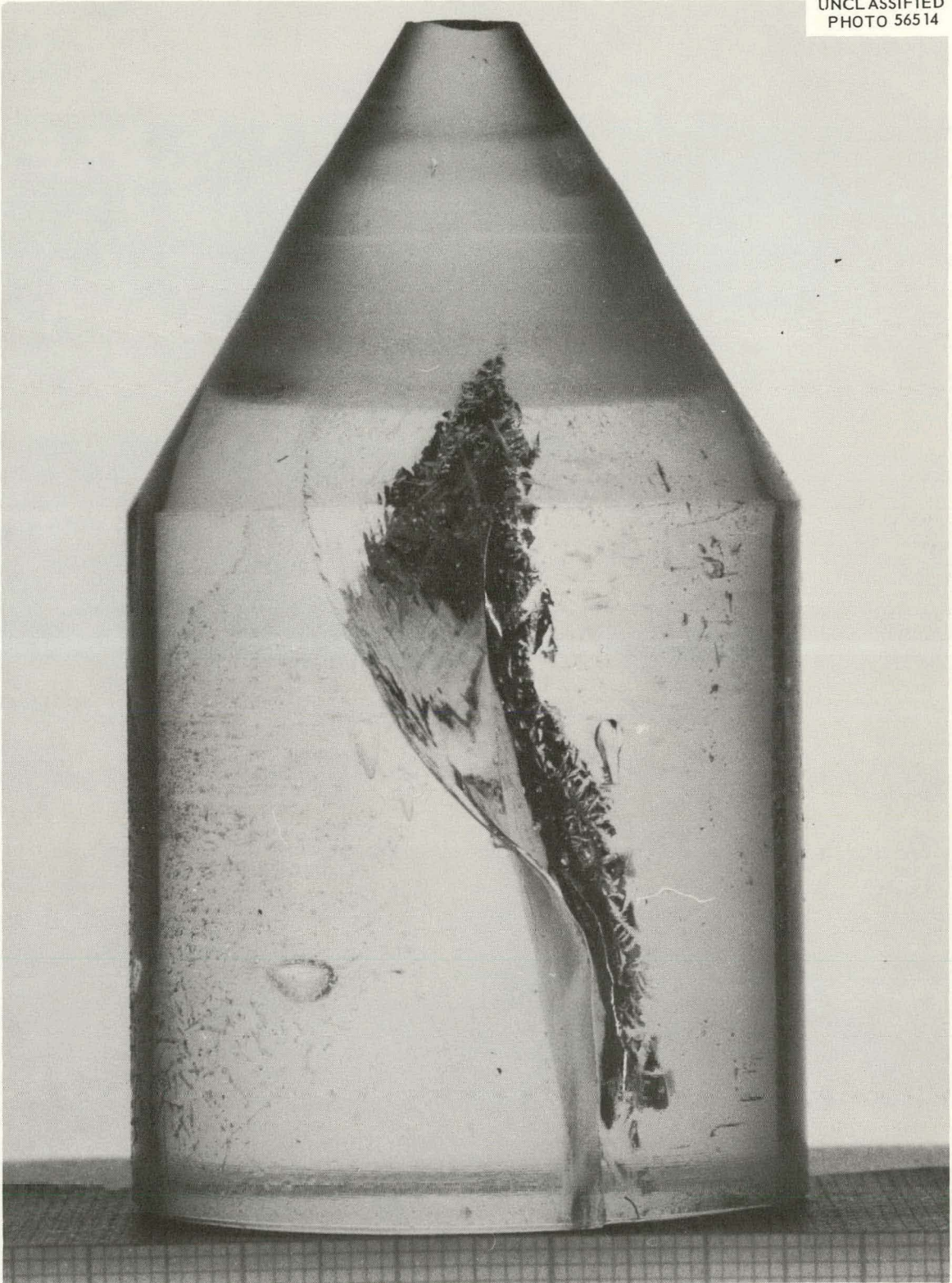
Fig. 7.   300-g LiF Bicrystal (99.99 at. % Li-7).

Fig. 8. Partly Sublimed LiF Charge at 830°C.

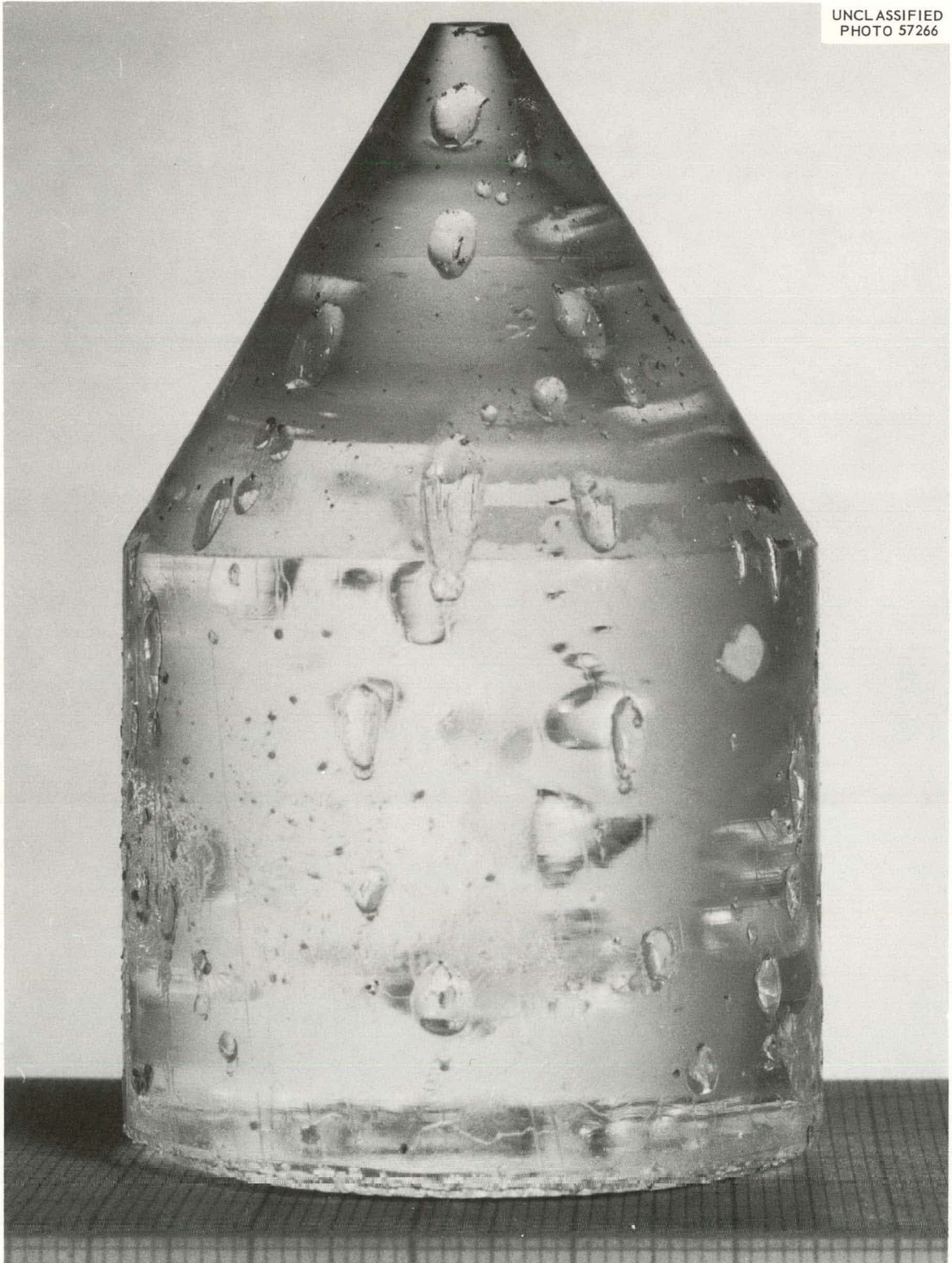Fig. 9. Crystal at 830°C Viewed Through Quartz Window.

Fig. 10. 200-g LiF Crystal (Showing Extensive Bubble Formation)
(99.99 at. % Li-7).

2. Some outgassing occurred. Pressure fluctuations were too
    small to be detected, but the required frequency of degas-
    sing the ion gage indicated outgassing of the melt. This
    observation, along with the absence of any cloudy region
    (the first ingot shown in Fig. 8 contained a cloudy region
    about 3 mm thick at the top of the ingot), indicates that
    vacuum melting is desirable as recommended frequently in
    the literature.

3. Remelting an ingot under an He atmosphere introduced bub-
    bles. These are seen in Figs. 7, 9, and 10. Few bubbles
    were observed in the first crystal (Fig. 7) produced from
    a charge which was melted under an He atmosphere but was
    not remelted. During the first melt the LiF charge was
    present as large chunks with numerous channels for gas to
    escape. Remelting occurred from a solid ingot without
    these channels, thus decreasing the possibility of He
    escape.

The fourth attempt to produce a crystal involved outgassing at 10^{-3}
to 10^{-4} mm until melting occurred. After 1 hr an He pressure of 1 to
1.5 atm was introduced into the capsule. While sublimation was negligible,
it was still observable under these conditions. About halfway through the
growth a few bubbles occurred, and an attempt was made to remove these bub-
bles by evacuating. When the pressure was reduced, gas was vigorously
evolved from the melt. The outgassing appeared to be successful, but after
completion of growth the ingot was found to be polycrystalline. It was
then remelted and the crystal shown in Fig. 11 was grown.

The fifth attempt failed because of a capsule rupture. The sixth and
seventh attempts produced the ingots shown in Figs. 12 and 13. The charge,
melted under a vacuum of 10^{-3} to 10^{-4} mm, was exposed to 1 to 1.5 atm of
helium after 1 hr. The crystal was grown and annealed under this pressure.
Before annealing, the thermal gradient (curves 1 and 2 of Fig. 14) was
eliminated (curve 3 of Fig. 14) by manipulating the external furnace shunts
(Figs. 2, A1, and A8). The annealing time was about 7 days with a low ini-
tial rate of cooling in order to make use of the high-temperature plasticity
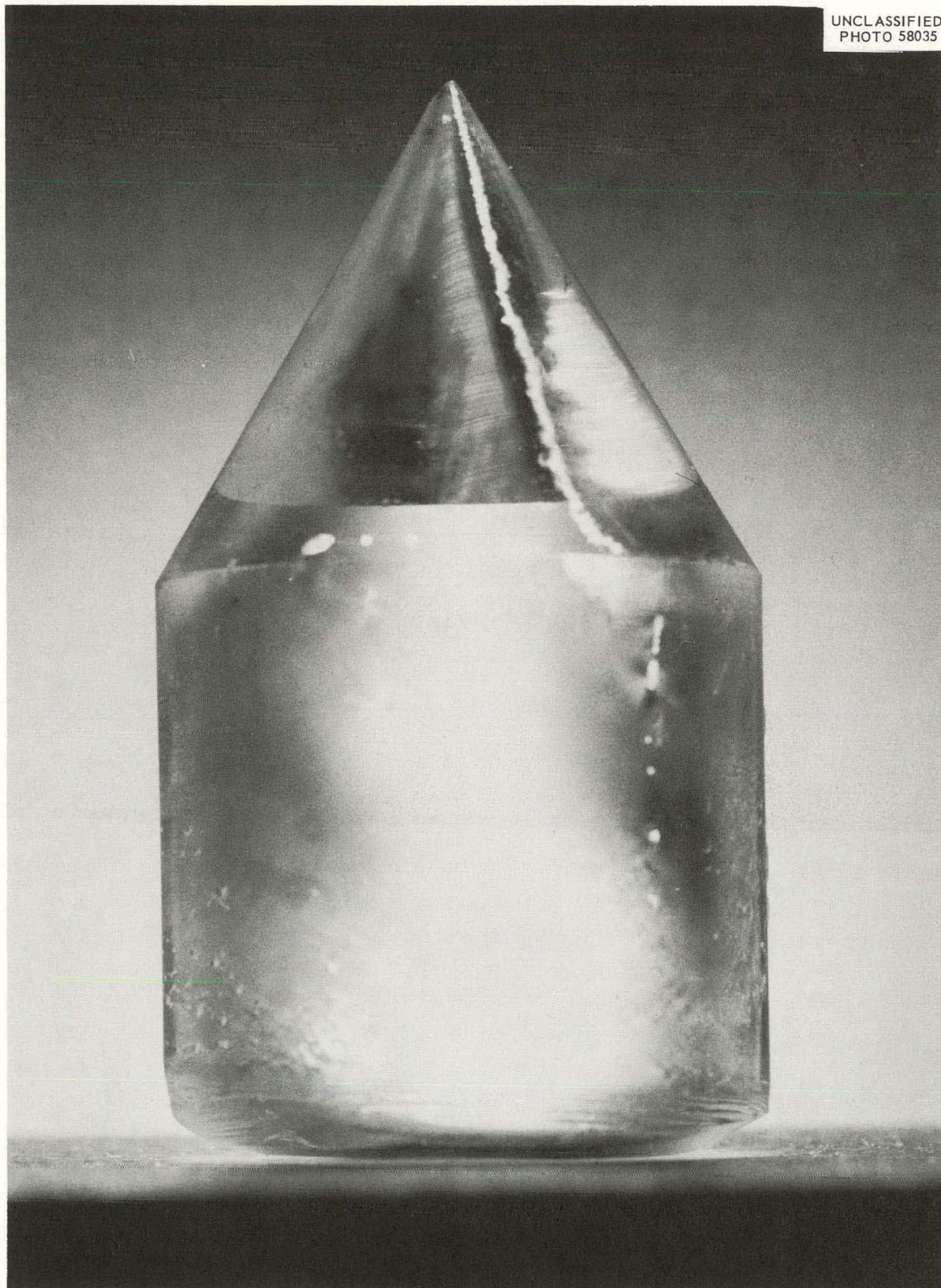
Fig. 11. 278-g LiF Crystal (98.06 at. % Li-7).
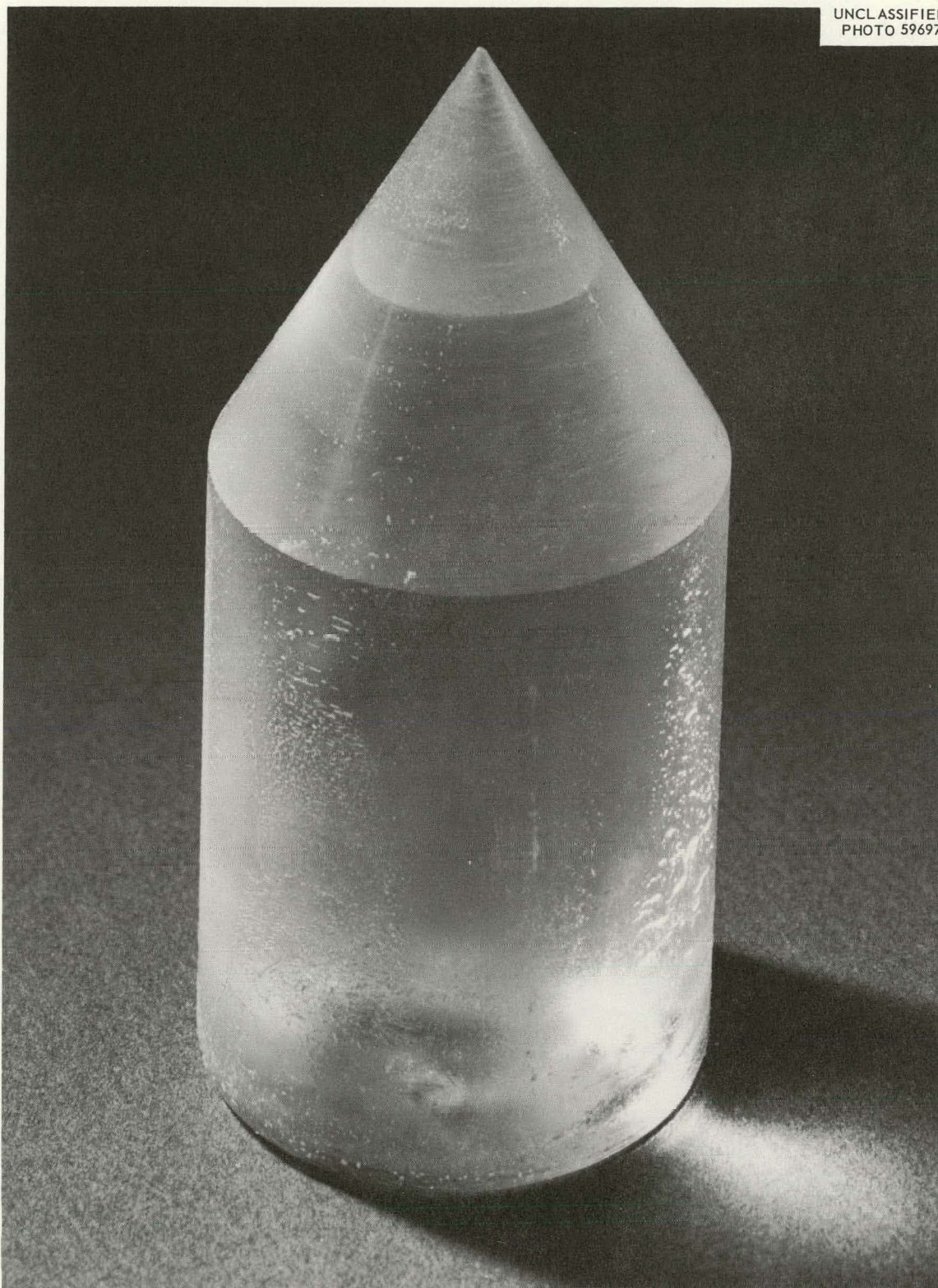
Fig. 12. 349-g LiF Crystal (99.99 at. % Li-7).
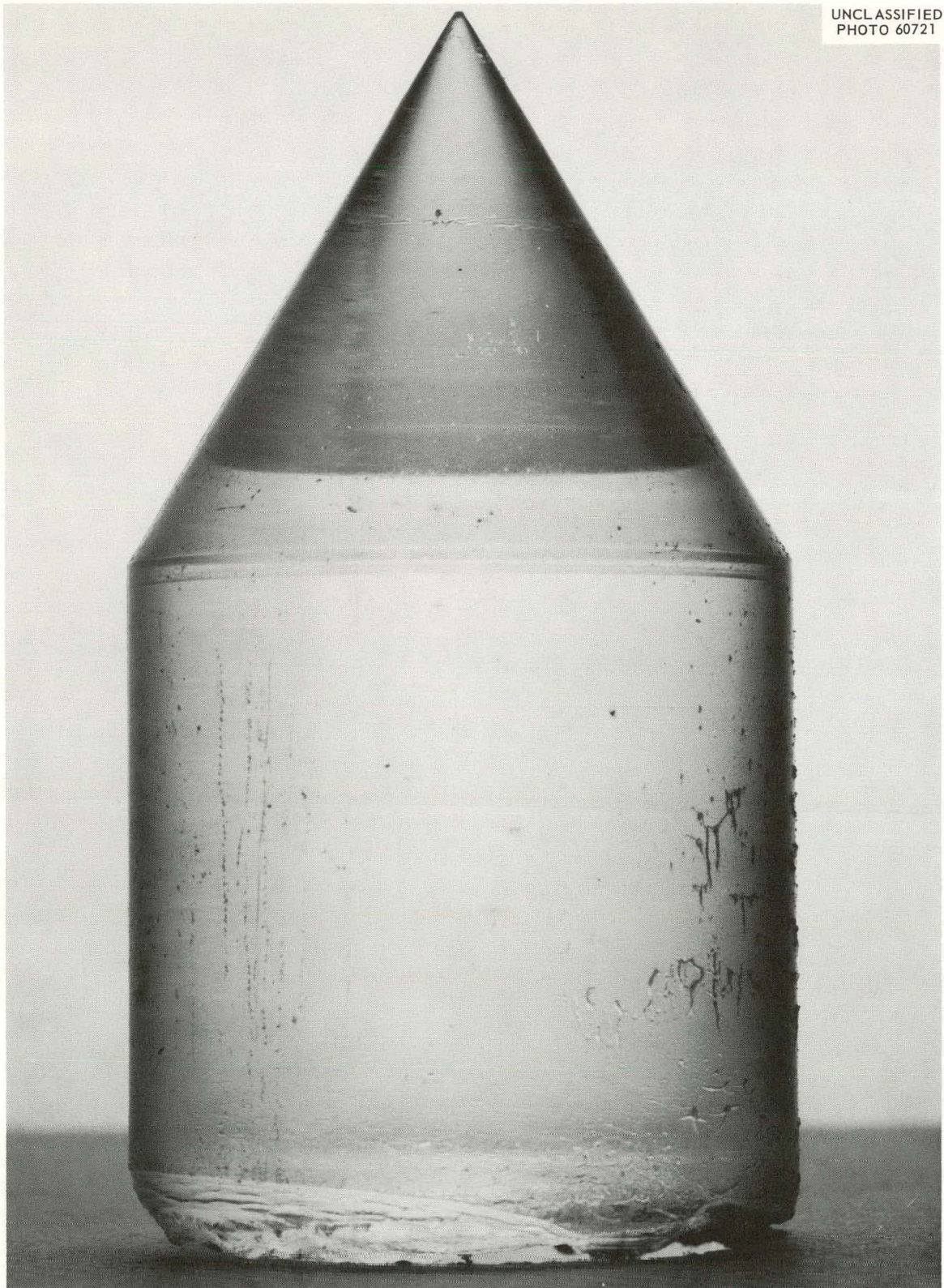
Fig. 13. 290-g LiF Crystal (96.50 at. % Li-7).

① CONTAINER TIP AT STARTING POSITION (CRYSTAL GROWTH CONDITION)
② CONTAINER TIP AT FINAL POSITION (CRYSTAL GROWTH CONDITION)
③ CONTAINER TIP AT 66.0 cm (CRYSTAL ANNEALING CONDITION)
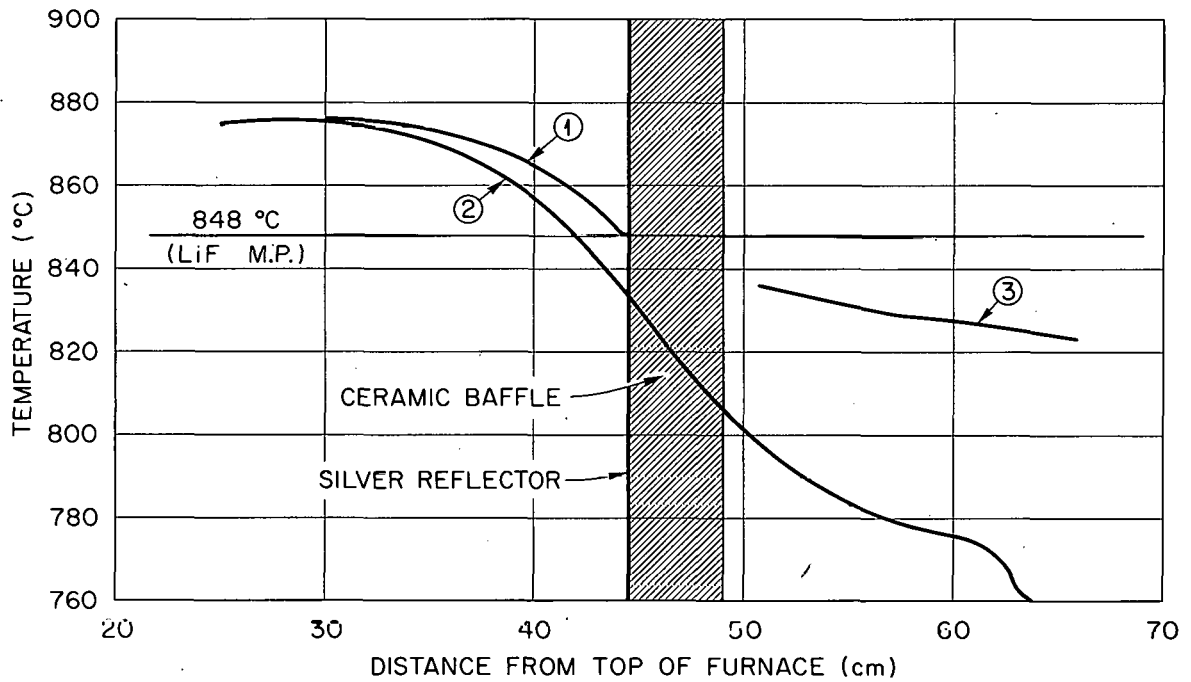
Fig. 14. Stockbarger-Bridgman Furnace Temperature Distribution.

of the LiF. The programmed cooling curve is shown in Fig. 15 in contrast
to the cooling curve obtained by simply shutting off the furnace power.
No internal strains were detected when the crystals were examined under
polarized light. Their infrared adsorption spectra were free of selective
absorption, thus indicating that the dehydration step was successful. The
results of the analyses of the first four crystals are given in Tables 2
and 3.

Table 2. Activation Analysis[a] of LiF

Material	Element (ppm)					
	Cu	K	Hg	Mg	Mn	Na
Heat-lamp dried LiF	2.7		73.1		0.1	
First crystal-middle[b]				3-7[b]	6-8[b]	
Second crystal-bottom					1.5	
Third crystal-bottom					1.4	
Fourth crystal-interior		≲0.2			0.13-0.35	0.01

[a]Analyses performed by E. I. Wyatt's group, except where stated
otherwise.

[b]Analyses performed at Cornell University - R. L. Sproull,
personal communication.

Distinctly higher concentrations of impurities were found near the
top of each crystal as was expected.[31] Also, a higher concentration of
Mn was found near the Ni-LiF interface, indicating that some leaching
occurred there. This suggests that future crystal-growth experiments
might produce a purer product if higher purity nickel, pyrolytic graphite,
or copper liners are used. Preliminary experiments indicate that copper
under an H_2 atmosphere will not contaminate molten LiF contained in it.
To withstand the hydrogen atmosphere at high temperature, the copper con-
tainers, including their welds, must be oxygen free.[45,46]

The strong dependence of purity on position in the crystals indicates
that zone melting should purify considerably the LiF. Work has been ini-
tiated in this direction.

Table 3. Spectroscopic Analysis[a] of LiF Crystals

Material	Element (ppm)										
	Ag	Al	B	Ca	Fe	K	Mg	Mn	Na	Si	Ti
First crystal-top		<100		20-50			50	70	100	<100	<100
First crystal-top middle		<100		20-50			100		50	100	<100
First crystal-bottom middle		<100		20-50			50		100		
First crystal-bottom				20-50			100		50		
Second[b] crystal-top		<10-300	nd[c]-500	30		20	20-50	<100-300	30	nd-200	
Second crystal-bottom		nd-<100		<10-20		20			10	nd-300[d]	100
Third crystal-top		<20					<10	20	<50		<20
Third crystal-bottom	<1				<1		<10	2	5		
Fourth crystal-interior								0.5-1			

[a] Analyses performed by J. A. Norris' group.

[b] Eleven analyses were performed on each portion of the second crystal. The range of results is shown in this table.

[c] Not detected.

[d] Of the eleven analyses, eight did not show Si, one gave <100 ppm, one 100 ppm, and one 300 ppm.
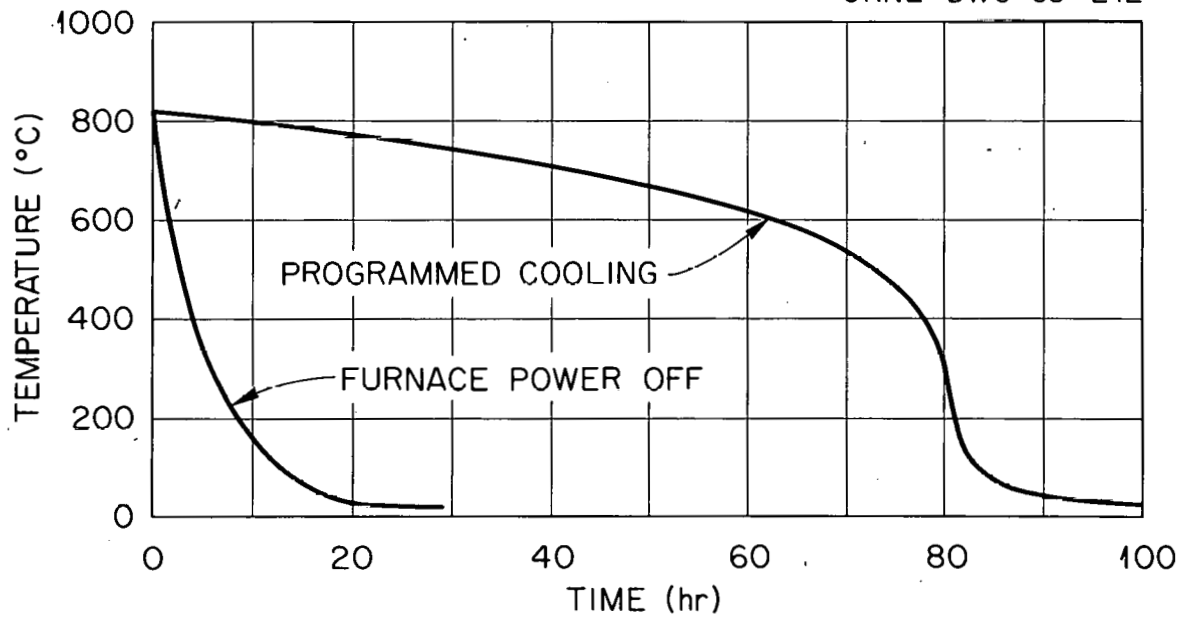
ORNL-DWG 63-212

Fig. 15. Stockbarger-Bridgman Furnace Cooling Curves.

Current oxygen analyses,[47] while relatively insensitive below 400 ppm in fluorides, indicate that the crystals produced thus far may contain 100 to 400 ppm of oxygen. Extent of oxygen removal is controlled by the equilibrium reaction, $2HF + Li_2O \rightleftharpoons H_2O + 2LiF$, and is therefore limited by the H_2O content of the HF, which is commonly estimated to be as high as 800 ppm in the "anhydrous" commercial product. From extrapolation of published vapor-phase data[48,49] for the $HF-H_2O$ system, liquid HF containing 800 ppm H_2O yields a vapor with only about 30 ppm H_2O. From the free-energy data[42] for the dehydration reaction, the calculated Li_2O content of the equilibrium product of the reaction with this vapor is only 10^{-7} ppm as compared to the analyzed concentration of 100 to 400 ppm. The oxygen values of 100 to 400 ppm may be due either to the difficulty in accurately analyzing at this concentration, introduction of oxygen after dehydration, or the inability to reach equilibrium readily. Consequently, further dehydration of LiF even with completely anhydrous HF may be very difficult. There are indications,[2] however, that repeated melting and freezing under vacuum will reduce the oxygen content of LiF. Consequently, the zone melting suggested above for removal of cationic impurities also may reduce the oxygen concentration. However, the proper evaluation of these procedures with respect to oxygen removal depends on a more sensitive oxygen analysis than is currently available.

Analytical results indicate that many impurities are selectively transferred during sublimation. It is clear, from the difficulties mentioned earlier with respect to sublimation, that moving large quantities of LiF by this means will be experimentally simple. An investigation of the feasibility of producing high-purity LiF by this method is in progress.

The problem of bubble formation, as mentioned earlier, depends on the inert-atmosphere pressures used but also seems to depend somewhat on the number of times that a particular capsule has been used. This may be a result of crystal growth of the Ni and the associated changes in the character of the surface of the capsule. The use of new capsule liners and of different materials should help to eliminate this problem.

The mosaic structure of these crystals is more pronounced than that of commercial material. This may be related to either epitaxial surface or vibration effects or to both effects. The epitaxial effects may be

cleared up by the changes in liner mentioned above. Reduction of capsule vibration during growth will be given attention.

The low-temperature thermal conductivity of these crystals is under study at the Materials Science Center at Cornell University. The high-temperature thermal conductivity is being studied at Oak Ridge National Laboratory.

The bottom portions of these crystals are being used to produce improved standards for spectroscopic analysis of LiF. In Tables 2 and 3 it can be seen that concentrations of impurities seem to decrease in order from the first to the fourth crystals. The first two crystals are now being reanalyzed using the new standards to determine if the trend in Table 3 reflects improved purity in the crystals or improved analysis. The calcium analysis in particular is noteworthy. Earlier analyses of the first and second crystals (Table 3) show 20 to 50 ppm calcium. Spectroscopic analysis at Cornell University, however, detected no calcium in the first crystal. The earlier reports of calcium impurity at ORNL are thought to have resulted from analytical problems which have been solved with the new standards. Spectroscopic analysis of crystals three and four do not show calcium.

ACKNOWLEDGMENTS

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Schematic Wiring Diagram & Apparatus Det.	D-56557
Furnace Liner Assembly And Details	D-56556
Packing Box, Packing Gland & Ring Details	D-56555
Crystal Capsule & Evacuation Line Details	D-56554
Quartz Window Assembly & Details	D-56553
Sections And Detail Sheet N.º 2	D-56552
Sections And Detail Sheet N.º 1	D-56551

LiF Crystal Growing Apparatus BLDG. NO. 4500-S

ASSEMBLY

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Fig. A1. LiF Crystal Growing Apparatus: Assembly.

Fig. A2. LiF Crystal Growing Apparatus: Sections and Details, Sheet No. 1.

Fig. A3.   LiF Crystal Growing Apparatus: Sections and Details, Sheet No. 2.

Fig. A4. LiF Crystal Growing Apparatus: Quartz Window Assembly and Details.
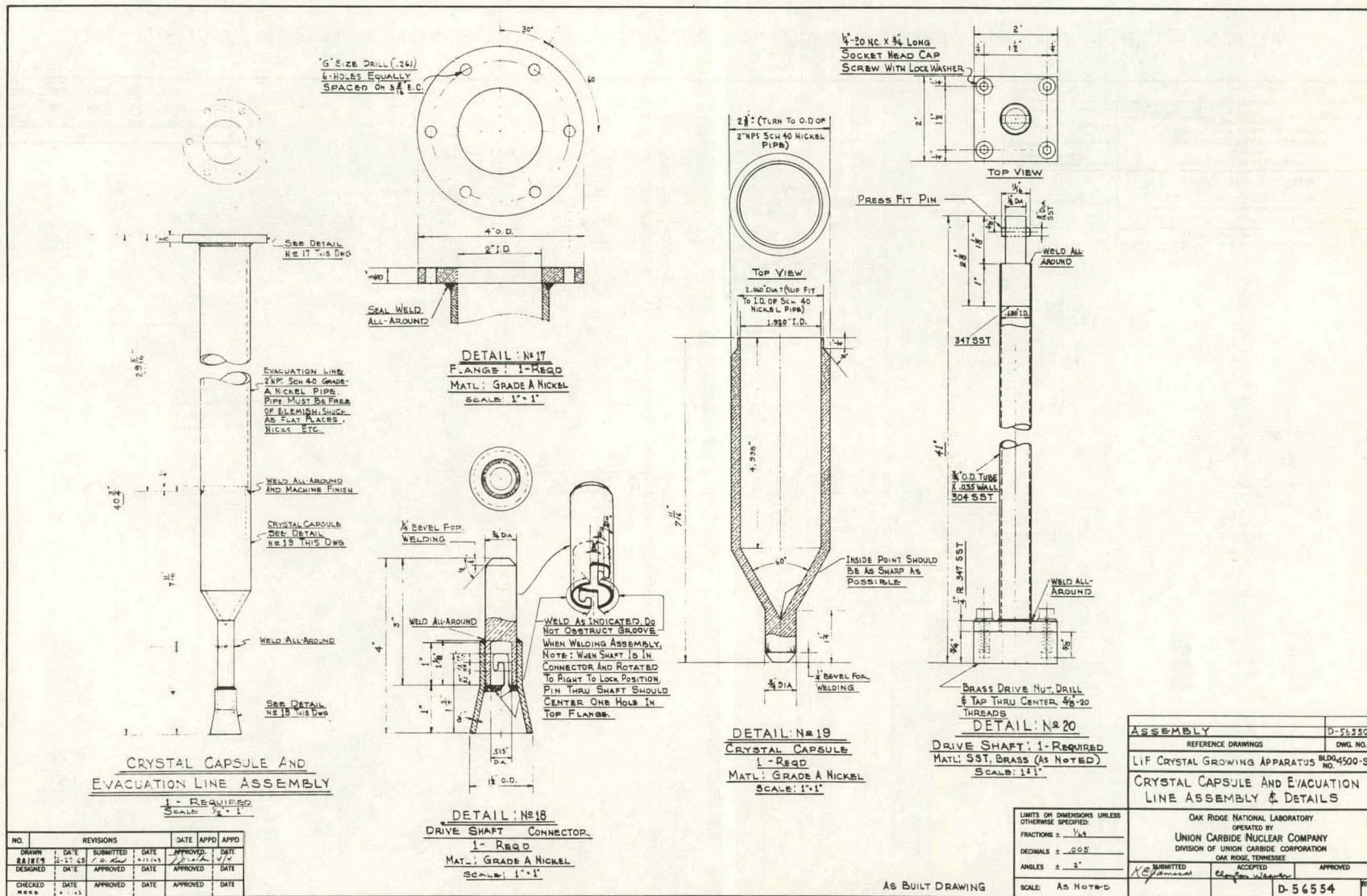
Fig. A5. LiF Crystal Growing Apparatus: Crystal Capsule and Evacuation Line Assembly and Details.
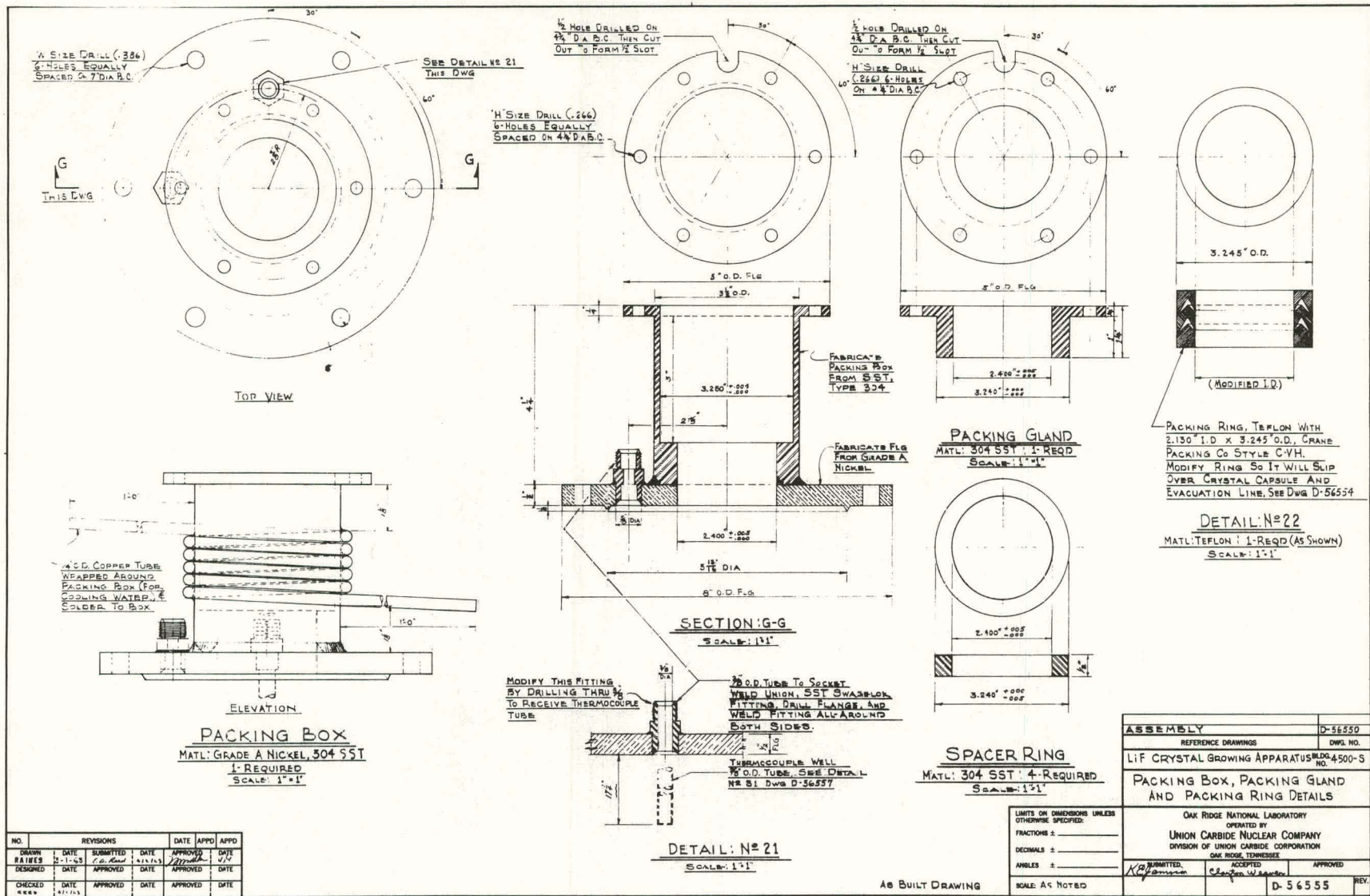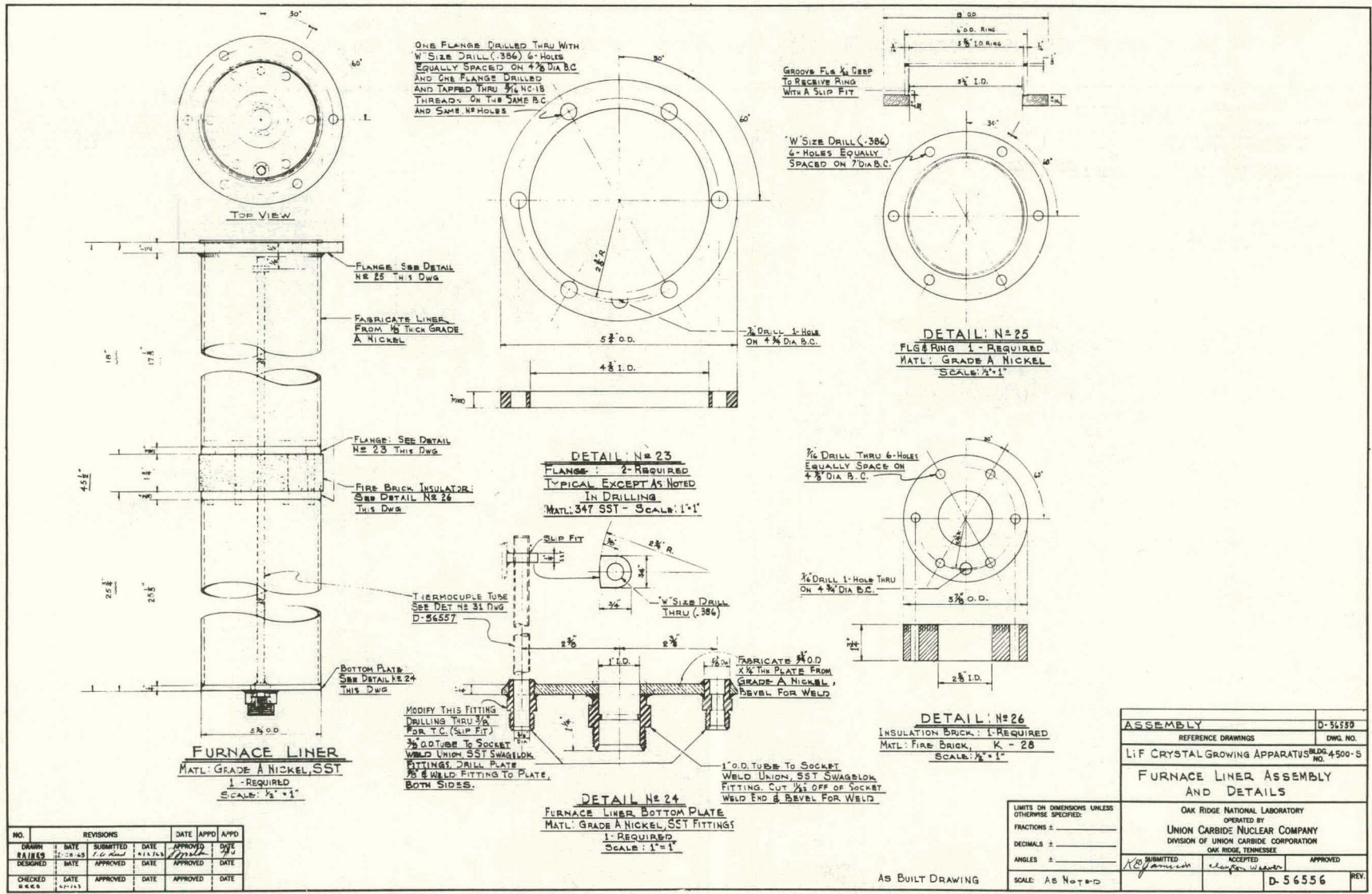
Fig. A6. LiF Crystal Growing Apparatus: Packing Box, Packing Gland, and Packing Ring Details.

Fig. A7. LiF Crystal Growing Apparatus: Furnace Liner Assembly and Details.

¼ O.D. Copper Tube Wrapped Around and Solder to 1"O.D. Tube

TOP VIEW

1" O.D. Tube x .062" Wall, 304 SST

1" O.D. Tube to Socket Weld Union, SST Swagelok Fitting, Cut off As Noted & Weld All Around 1" O.D. Tube

1" to ¾" O.D. Tube Adapter, See Det No 28 This Dwg

DETAIL: № 27
Drive Shaft Cooling Coupling
Matl: SST : 1-Required
Scale: 1"-1"

1¼ Dia

¾" O.D.

1" O.D.

DETAIL: № 28
1" to ¾" O.D. Tube Adapter
Matl: Teflon : 1-Required
Scale: 1"-1"

¼ Drill 2-Holes

DETAIL: № 29
Liner Hold Down Clamp: 1-Reqd
Matl: 304 SST
Scale: ½"-1"

TOP VIEW

¾"R (Top)

DETAIL: № 30
Cold Trap Support Stool
Matl: Aluminum : 1-Required
Scale: 3"-1'0"

Seal End of Nickel Tube

⅜" O.D. Tube x .035 Wall Grade A Nickel

"A"

⅜" O.D. Tube Hex Head Nut With Pressure Seal Fitting (Swagelok, SST) To Fasten To Fittings Shown In Details 21 Dwg D-56555 & 24 Dwg D-56556

DETAIL: № 31
Thermocouple Tube: 2-Req'd
Matl: Grade A Nickel - Scale: 1"-1"

Thermocouple Tube	"A"
To Fit Up Into Furnace Liner	48"
To Fit Down Into Packing Box	21"

Input Voltage 0-220V From Control Panel

Rheostat Connection Typical For 18

10 ft, 5.58 Amps

From 110 Volt Supply

Furnace Heating Coil With 22 Connecting Posts

SCHEMATIC WIRING DIAGRAM of High Temperature Furnace

ASSEMBLY	D-56550
REFERENCE DRAWINGS	DWG. NO.
LiF Crystal Growing Apparatus	BLDG. NO. 4500-S
SCHEMATIC WIRING DIAGRAM AND APPARATUS DETAILS	

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Fig. A8. LiF Crystal Growing Apparatus: Schematic Wiring Diagram and Apparatus Details.

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