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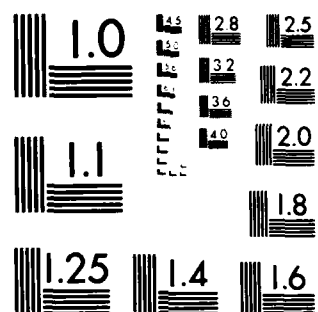   ZONE TECHNIQUE(U) EIC CORP NEWTON MASS R D RAUH ET AL.
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Report N00014-82-C-0629

GROWTH OF Ce^{+3} DOPED OXIDES BY THE
TRAVELING SOLVENT ZONE TECHNIQUE

R. David Rauh, Kenneth D. Brady,
Tom A. Kavassalis and David H. Longendorfer

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June 1983

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

    Preliminary experiments have been carried out to determine the feasibility of flux growth of Ce^{+3} doped $La(Al,Sc)O_3$ using the traveling solvent zone technique. In particular, a new cubic host lattice, $LaAl_{0.7}Sc_{0.3}O_3$, was prepared by arc furnace techniques and found to have expanded lattice dimensions compared to $LaAlO_3$. The mixed perovskite has a more ideal A:B radius ratio than $LaAlO_3$ perhaps promoting more ideal cubic symmetry.

20. Abstract (Cont.)

Flux syntheses were unsuccessful in producing single crystals of $LaAlO_3$ or $La(Al,Sc)O_3$. Reducing or neutral fluxes were stressed to prevent oxidation of Ce^{+3} dopant to Ce^{+4}. A pure KF flux promoted the reaction of Al_2O_3 and La_2O_3 to form $LaAlO_3$. The addition of Sc_2O_3 to the flux mixture appeared to result in a garnet phase, analogous to the compound $La_3Sc_2Ga_3O_{12}$, whose X-ray structure is known.

A TSZ crystal growing furnace was constructed, using resistively heated components capable of a hot zone temperature of $\sim 1400°C$. Problems were encountered in high rates of flux volatilization and corrosion of the furnace and boules. Hence, it was concluded that a totally encapsulated and sealed growth system would be required.

A theoretical component of the program entailed development of a crystal field program written in Fortran for the IBM personal computer, in order to help interpret host lattice effects of Ce^{+3} d → f luminescence.

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INTRODUCTION

Optical communications through seawater can be achieved with sources centered at $\sim$480 nm, the blue-green spectral region. Therefore, crystals exhibiting blue-green luminescence are of considerable interest as solid state lasers. Particular attention has been focused on the Ce^{+3} d $\rightarrow$ f luminescent transition, which is broad and appears to center around 520 nm in $Y_3Al_{12}O_{15}$ (YAG).[1,2] The coordination in YAG has Ce^{+3} occupying the center of a cube of O^{2-} ions. In other lattices such as $ScBO_3$, where Ce^{+3} is coordinated octahedrally by $6O^{2-}$ ions, emission is typically observed in the UV at λ <420 nm.[2] Blasse and Bril[2] observed that these symmetry sensitive luminescence spectra are in keeping with simple considerations of crystal field theory. Unfortunately, Ce^{+3}-YAG appears to be an unsuitable blue-green laser material because the emission is at too low an energy, and because of parasitic excited state absorption processes which, although not well-understood, preclude laser action.[3]

These accumulated results have led to a search for alternative oxide hosts incorporating Ce^{+3} in a cubic 8-fold (or higher) coordination. Two new materials have come to our attention. One is ThO_2, in which Ce^{+3} would have cubic site symmetry, but in which there would be a strong tendency for isovalent substitution. However, our measurements on small flux-grown crystals of Ce^{+3} doped ThO_2[4] using pulsed N_2 laser excitation (337.1 nm) show a broad luminescence with λ_{max} $\sim$480 nm. The other host material, $LaAlO_3$, shows an absorption onset of $\sim$440 nm when doped with Ce^{+3}.[2] This would place the d $\rightarrow$ f luminescence in approximately the correct spectral range. The Ce^{+3} would have a dodecahedral O^{2-} coordination in this crystal. We have demonstrated a flux synthesis of $LaAlO_3$ (to stabilize the cubic structure), using La_2O_3, Al_2O_3, and CeF_3 as reactants and 2 m/o $BaCO_3$ and BaF_2 as flux. The reaction is carried out at 1150°C in air in a Pt crucible. Some indication of blue-green luminescence in Ce^{+3} doped $La(Al,Sc)O_3$ has been observed recently.[5]

A critical factor in all of these investigations is the growth of single crystals of these highly refractory host materials. Growth of ThO_2 and $LaAlO_3$ can be achieved using a suitable flux, but the crystals so obtained are of irregular shape and must be separated from the surrounding flux after cooling.

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[1] G. Blasse and A. Bril, Appl. Phys. Letters 11, 53 (1967).

[2] G. Blasse and A. Bril, J. Chem. Phys. 47, 5139 (1967).

[3] W. Miniscalco, J. Pellegrino and W. Yen, J. Appl. Phys. 49, 6109 (1978).

[4] W. Zwicker et al., ONR Final Technical Report, Contract N00014-79-C-0180, October 1982.

[5] V. Nicolai, Office of Naval Research, private communication.

In order to achieve a more controlled growth of these crystals by the flux method, the traveling solvent zone (TSZ) technique might be employed. Table 1 lists some oxides which have been grown by this method. A simple apparatus for crystal growth using this procedure is shown in Figure 1. The reactants are contained in a boule with a pointed tip to enhance crystal nucleation. Initially, the flux is contained within the tip of the boule. Above it is a rod of feedstock (e.g., Ce^{+3} doped $LaAlO_3$) which has been pressed and sintered into a dense ceramic rod. A hot zone is defined by an independently controlled heating element. As the boule is lowered through the hot zone, dissolution of the feedstock occurs at the upper flux/ceramic interface while crystallization of the oxide occurs at the bottom (existing) interface. The role of "background" heating is uncertain, but may be necessary here to maintain a hot zone temperature above ∿1300°C, if required; thus, it is included in Figure 1.

TABLE 1. CRYSTALS OF OXIDES GROWN BY THE TRAVELING SOLVENT ZONE METHOD

Material	Flux	T(background) (°C)	T(growth zone) (°C)	Growth Rate (mm/hr)	Ref.
$BaTiO_3$	TiO_2	1290	1350	0.1	6
$CaCO_3$	Li_2CO_3	ambient	750	0.2	7
ZnO	PbF_2	ambient	900	0.15	8
$SrTiO_3$	PbF_2/PbO	ambient	1250	0.05	9
$(Pb,Sr)TiO_3$	PbF_2/PbO	ambient	1100	0.05	9
$PbTiO_3$	PbF_2/PbO	ambient	1075	0.05	9

In this program, we have evaluated several fluxes for growth of $LaAlO_3$, $LaAl_{1-x}M_xO_3$ (M = Sc^{+3}, Ga^{+3}) and $LaScO_3$ containing Ce^{+3}, and have compared the products to those synthesized in a high temperature arc furnace. A TSZ crystal growing furnace has been designed and constructed, and some preliminary flux growth runs carried out. Modifications to the crystal growth apparatus have been suggested based on the results.

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[6] C. E. Turner, N. H. Mason and A. W. Morris, J. Crystal Growth 56, 137 (1982).

[7] J. J. Brissot and C. Belin, J. Crystal Growth 8, 213 (1971).

[8] G. A. Wolff and H. E. LaBelle, Jr., J. Am. Ceram. Soc. 48, 441 (1965).

[9] B. DiBenedetto and C. Cronan, J. Am. Ceram. Soc. 51, 364 (1968).
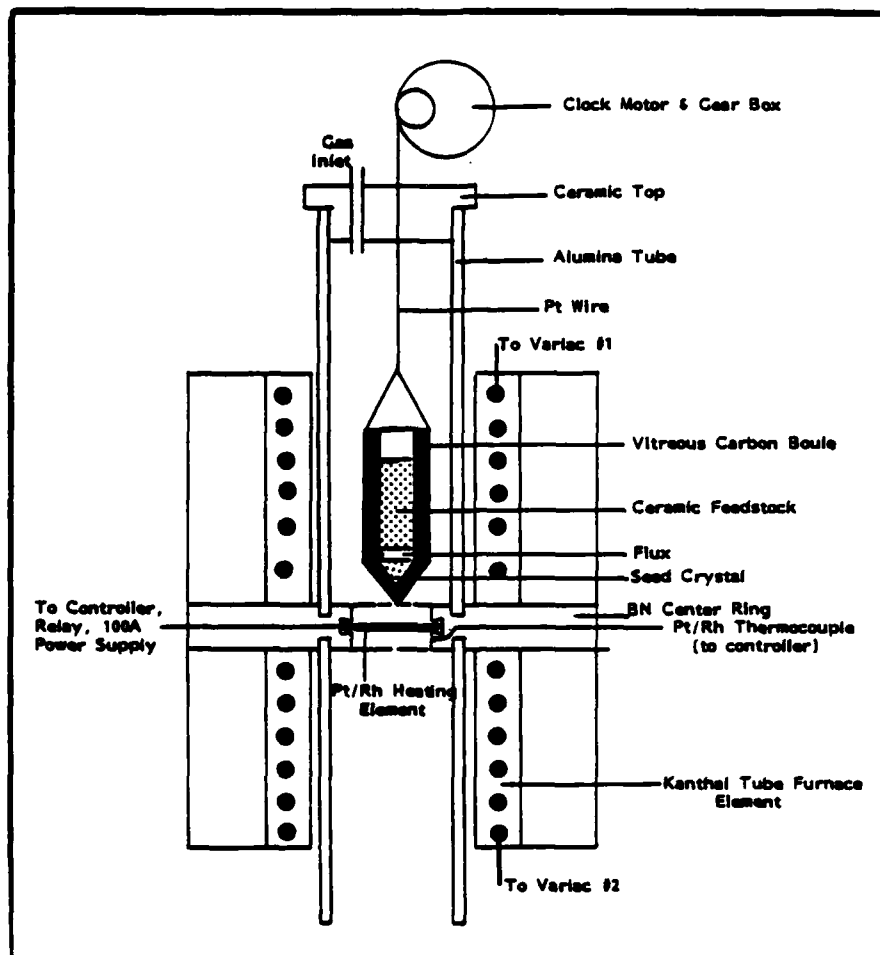
Figure 1. Furnace and boule arrangement for controlled growth
of oxide crystals from flux by the traveling solvent
zone technique.

As a parallel project, a computer program has been written for a
IBM personal computer that performs simple crystal field calculations
with the input of various lattice parameters. It is anticipated that
such a program will be useful in interpretation of host dependent Ce^{+3}
absorption and luminescence spectra. It is reproduced, with documenta-
tion, in the Appendix.

5

RESULTS

Oxide Syntheses using Arc Furnace Techniques

In order to incorporate Ce^{+3} into a perovskite lattice, and at the
same time avoid partial oxidation to Ce^{+4}, the synthetic reactions must
be carried out under neutral or reducing conditions. One convenient
method for such synthesis is to employ an arc furnace. The furnace is
supplied commercially by Centorr Assoc., Suncook, NH, and is essentially
the same design as described by Reed and Pollard[10],[11], the originators of
the technique. The furnace body consists of a thoreated tungsten cathode
centered above a water cooled graphite or copper hearth, which also serves
as the anode. The arc is struck using a conventional welding power supply
(300 amp, 30V). The cathode and hearth are encased within a quartz window
sleeve, compression sealed to the top and bottom against O-ring gaskets.
The cathode is attached to a handle which protrudes through the top, held
by a ball and socket joint which permits adjustment of the arc angle. Gas
purge tubes are introduced into the top and base, so that the furnace can
be operated either in vacuo or under a chosen atmosphere - usually reducing,
unless cathode and anode materials are employed with high temperature oxida-
tion resistance (e.g., Ir).

In actual operation, the components of the material to be synthesized
are introduced into a depression in the hearth. After flushing the chamber
and introducing the desired atmosphere, the arc is struck and directed into
the feedstock. The current is increased until melting occurs. Since the
hearth is water cooled, the molten charge "beads up", forming a thin skin
of solid material at the interface. All of the powder in the hearth may
be guided into the bead by manipulating the arc position. The cold hearth
minimizes contamination of the charge - thus, a containment material such
as Cu may be employed, because of its excellent thermal conductivity.

The arc furnace methods were used for attempted syntheses of $LaAlO_3$,
$LaAl_{0.7}Sc_{0.3}O_3$ and $LaScO_3$, containing 0.1 to 1.0 mole % Ce^{+3}, added as
Ce_2O_3. The mixtures were prepared stoichiometrically from the component
oxides. These were ultimately mixed and ground for several hours using
an agate mortar in the presence of MeOH, to form a jewelers' paste. The
MeOH was subsequently stripped in a vacuum oven at 100°C. The resulting
powder was cold pressed into pellets for introduction into the arc furnace
(typically ~10g per run). All runs were conducted in an Ar atmosphere.

All materials prepared in the arc furnace possessed a grey colora-
tion, independent of the hearth used. If the reaction time was too short,

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[10]T. B. Reed, Mat. Res. Bull. 2, 349 (1967).
[11]T. B. Reed and E. R. Pollard, J. Cryst. Growth 2, 243 (1968).

there was a tendency for the solidified bead to form a "geode," with an
unreacted powder encased in a hard, amorphous appearing shell. Thus,
a reaction time of at least 10 minutes was necessary to ensure complete
reaction. The homogeneity was further promoted by stopping the fusion,
turning over the bead, and resuming the arc melting on what was the
bottom surface. (These techniques were practiced first by us in the
laboratory of Mr. Robert Fahey[12], at the MIT Lincoln Laboratories, before
being conducted on our own apparatus.)

Samples prepared by the arc furnace technique were either non-
luminescent or only very weakly so, independent of the Ce content.

The X-ray diffraction patterns of the products are summarized in
Figure 2. The $LaAlO_3$ arc synthesis led unequivocally to the desired
product, with no X-ray observable contaminants (detection level <0.5%).
This was reproduced in several separate runs carried out both at Lincoln
Laboratories and at EIC. The $LaScO_3 \cdot 0.1\%$ Ce synthesis led to a product
with a more complex X-ray pattern than that of the nearly cubic $LaAlO_3$.
The pattern contained the lines attributable to $LaScO_3$ in the orthorhombic
$GdFeO_3$ structure. Several impurity peaks were unassigned, but appear
consistent with Sc_2O_3. Definite assignment is difficult due to overlap
between most of the major $LaScO_3$ and Sc_2O_3 peaks. La_2O_3 was definitely
not present in the product.

Syntheses of $LaAl_{0.7}Sc_{0.3}O_3$ were carried out with 1% and 0.1% Ce^{+3}
added. The X-ray patterns of the products are of a simple cubic structure.
As seen in Table 2, comparison with $LaAlO_3$ indicates that the mixed oxide

TABLE 2. X-RAY DIFFRACTION PARAMETERS MEASURED FOR
ARC FURNACE SYNTHESIZED $LaAlO_3$ AND $LaAl_{0.7}Sc_{0.3}O_3$

$LaAlO_3$	$LaAl_{0.7}Sc_{0.3}O_3$	hkl
d(A)	d(A)	
3.71	3.86	012
2.64	2.70	110
2.17	2.21	202, 006
1.88	1.91	024
1.68	1.71	122, 116
1.54	1.57	300, 214, 018
1.33	1.36	220, 208

has a more expanded lattice, as would be expected for the substitution of
Sc^{+3} (r = 0.81A) for Al^{+3} (r = 0.50A). Again, the Ce^{+3} doped material
was only very weakly fluorescent, yielding a luminescence spectrum similar

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[12]T. B. Reed, R. E. Fahey and J. M. Honig, Mat. Res. Bull. <u>2</u>, 561
(1967).
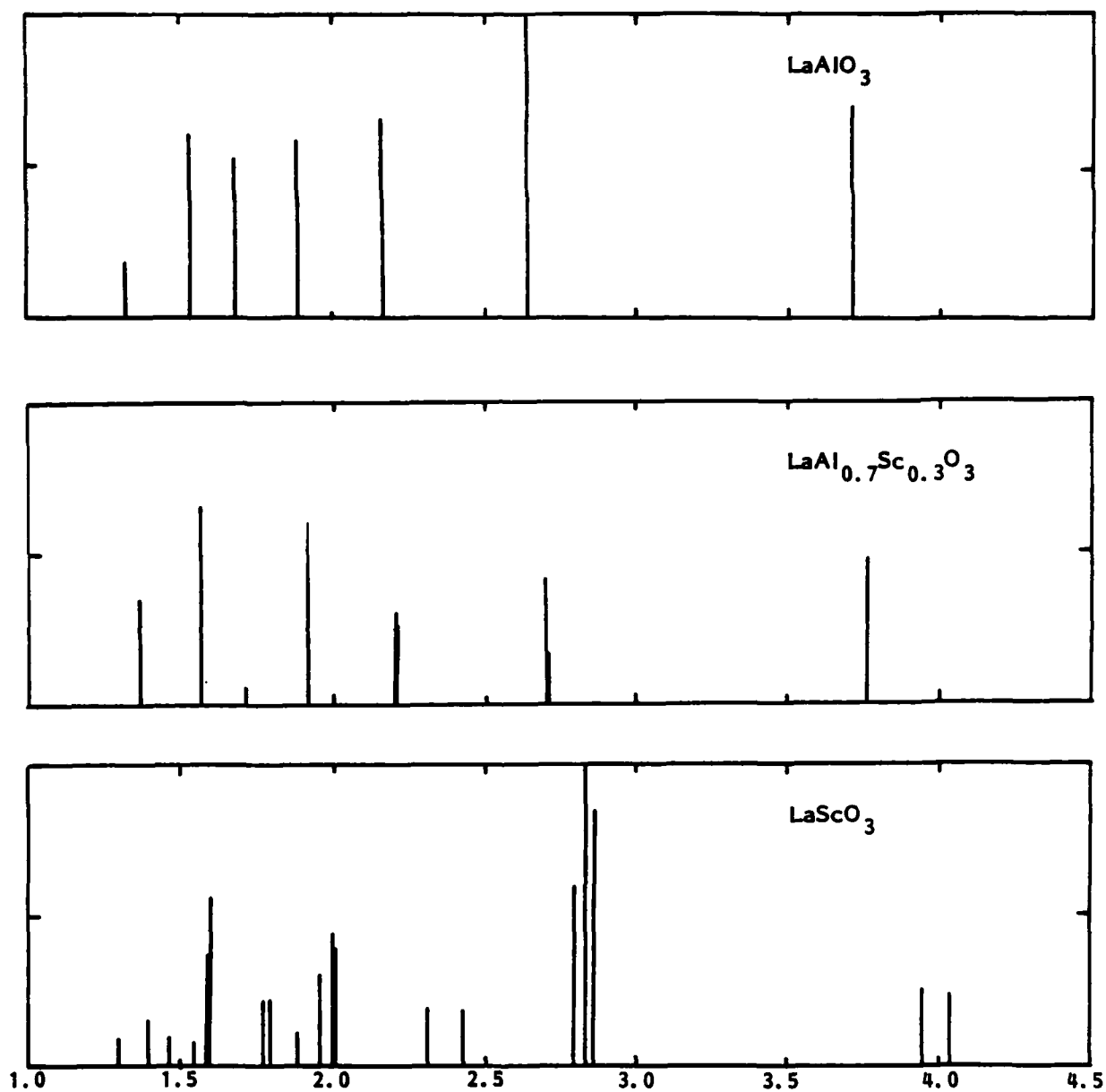
Figure 2. X-ray diffraction patterns of La oxides prepared in an arc furnace under Ar from mixtures of the component oxides. The LaAlO$_3$ spectrum is in good agreement with the literature.

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to that reported earlier[13] (λ_{max} = 450 nm). However, since the products were grey, they apparently contained considerable concentrations of C or reduced impurity that could lead to luminescence quenching. From a structural viewpoint, the mixed La(Sc,Al)O_3 matrix would appear to be an interesting lattice for accommodating Ce^{+3} in a cubic environment.

Oxide Syntheses from Fluxes

For TSZ crystal growth, it was first necessary for us to survey several potential flux solvents for synthesis of LaAlO$_3$ and La(Al,Sc)O$_3$. These experiments were conducted in a Lindburg muffle furnace with a controlled atmosphere retort. The temperature was lowered at a pre-determined rate by a clock motor driven gear mechanism attached to the rheostat of the temperature controller. Syntheses were conducted in 20 ml Pt crucibles with mechanically fitted tops (Engelhard Corp.).

In general, fluxes were selected which were molten below ~1400°C, the upper temperature limit of our furnace apparatus. This is also the probable upper temperature limit that the hot zone of a boule lowered through our TSZ furnace could be expected to attain homogeneously (see below). It is also of interest to seek low temperature growth of LaAlO$_3$ single crystals, in order to avoid the twin-producing cubic to tetragonal phase transition at 450°C.[14]

Representative fluxes and conditions of syntheses are summarized in Table 3. In all cases, the starting materials consisted of mixtures of the component oxides (e.g., La$_2$O$_3$, Al$_2$O$_3$ and Ce$_2$O$_3$) plus a molar excess of the flux. The ratio of feedstock material to flux was chosen according to various literature sources for flux growth of perovskite crystals.[6-9]

The BaF$_2$/BaCO$_3$ flux (not shown in Table 3) did not melt at the reaction temperature. This material does, however, promote the solid state reaction of La$_2$O$_3$ and Al$_2$O$_3$ to yield LaAlO$_3$. We have previously reported the synthesis of blue-green luminescent Ce^{+3}-doped LaAlO$_3$ using this technique.[13]

The two oxide fluxes, Na$_2$B$_4$O$_7$ and 4Bi$_2$O$_3$·V$_2$O$_5$, did form a molten flux. The components of the desired compound (e.g., La$_2$O$_3$, Al$_2$O$_3$, etc.) were mixed with the flux by intimate grinding with an agate mortar in a MeOH paste. The mole percent of flux in these syntheses was between

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[6]Turner et al., loc. cit.

[7]Brissot and Belin, loc. cit.

[8]Wolff and LaBelle, loc. cit.

[9]DiBenedetto and Cronan, loc. cit.

[13]R. D. Rauh and A. N. Scoville, ONR Final Technical Report, Contract N00014-82-C-0142, July 1982.

[14]J. P. Coutures, J. M. Badi, R. Berjoan, J. Coutures, R. Flamand and A. Rouanet, High Temp. Science 13, 331 (1980).

TABLE 3. CONDITIONS FOR OXIDE SYNTHESES FROM FLUXES.

Oxide Composition	Flux Composition	Flux: Oxide Molar Ratio	Growth Conditions	Extraction	Product Description
1:1 La_2O_3, Al_2O_3 0.1 M/o CaF_3	4:1 Bi_2O_3, V_2O_5	1:1	1350°C for 3 h; 1350→900°C at 5°/h	6N HCl	Clear crystalline plates, 1-2 mm. Blue fluorescence; pink fluorescing impurities.
1:1 La_2O_3, Al_2O_3 0.05 M/o Ce_2O_3	4:1 Bi_2O_3, V_2O_5	1:1	1350°C for 4 h; 1350→900°C at 10°/h	50% HNO_3	Clear crystalline plates; weak blue fluorescence.
1:0.7:0.3 La_2O_3, Al_2O_3, Sc_2O_3 0.05 M/o Ce_2O_3	4:1 Bi_2O_3, V_2O_5	1:1	1350°C for 4 h; 1350→900°C at 1°/h	50% HNO_3	Yellow powder; weak green fluorescence.
1:1 La_2O_3, Al_2O_3 0.05 M/o Ce_2O_3	$Na_2B_4O_7$	2:3	1250°C for 20 h; 1250→850°C at 3.3°/h	50% HNO_3	White powder; no fluorescence.
1:1 La_2O_3, Al_2O_3 0.5 M/o Ce_2O_3	$Na_2B_4O_7$	3:2	1250°C for 16 h; 1250→850°C at 3.5°/h	6N HCl	All products dissolve in HCl.
1:0.7:0.3 La_2O_3, Al_2O_3, Sc_2O_3 0.1 M/o Ce_2O_3	$Na_2B_4O_7$	3:2	1250°C for 16 hr; 1250→850°C at 3.5°/h	6N HCl	Fine white needles, no fluorescence.
1:1 La_2O_3, Al_2O_3 0.4 M/o Ce_2O_3	KF	3:25	1050°C for 24 h; 1050→770°C at 20°/h (Ar atmosphere)	6N HCl	White product dissolves in HCl.
1.67:1 La_2O_3, Al_2O_3 0.4 M/o Ce_2O_3	KF	3:25	1050°C for 24 h; 1050→770°C at 20°/h (Ar atmosphere)	6N HCl	White powder; no fluorescence.
1:0.67:0.33 La_2O_3, Al_2O_3, Sc_2O_3 0.4 M/o Ce_2O_3	KF	3:25	1050°C for 24 h; cool 1050°C for 3 h; 1050→770°C at 20°/h (Ar atmosphere)	6N HCl	White powder; no fluorescence.

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40 and 60%. The oxide-flux mixtures were allowed to equilibrate at the
upper temperature (1200 to 1400°C) for several hours before cooling at
3-20°C/hr to a temperature near the flux solid function (750-900°C).
Then, the fluxes were either rapidly quenched or poured off any product
as a melt. The reactions with these oxide fluxes were all conducted in
an air atmosphere.

X-ray diffraction patterns of the products of the oxide flux reac-
tions indicated that Al_2O_3 was a major product component, and that $LaAlO_3$
and $LaScO_3$ were minor components, if present at all. For the most part,
the products of the flux reactions had different X-ray diffraction patterns
from the arc-furnace prepared materials. Although there were some similar-
ities between the X-ray patterns of the $4Bi_2O_3 \cdot V_2O_5$ flux products and that
of $LaAlO_3$, several peaks are missing or shifted, so that positive identifica-
tion is questionable. The X-ray pattern of this product is shown in Figure 3.

KF also remained molten throughout the reaction temperature range.
The X-ray pattern of the product of the reaction of La_2O_3 and Al_2O_3 in KF
was identical to that produced in the arc furnace synthesis, and is iden-
tified as $LaAlO_3$. The product was a white powder and did not fluoresce
despite the fact that the reaction was carried out under Ar. The sample
of $LaAl_{0.7}Sc_{0.3}O_3$, 1% Ce prepared in a KF flux had a complicated X-ray
spectrum, but only one dominant line at d = 2.84Å. The spectrum, shown
in Figure 4, is similar to that of the garnet $La_3Sc_2Ga_3O_{12}$, which can be
prepared from the solid state reaction of La_2O_3, Sc_2O_3 and Ga_2O_3. This
type of phase is not unlikely in the present case, since Al^{+3} and Ga^{+3}
often substitute isostructurally.

Several experiments were conducted on growth of $LaAl_{1-x}Ga_{1-x}O_3$
using the fluoride and oxide fluxes. However, weighing the crucible
before and after the syntheses indicated that the Ga_2O_3 had been lost
to volatilization. Hence, no further experiments were performed on this
system.

Traveling Solvent Zone Experiments

1. __Furnace Design and Assembly.__ The traveling solvent zone
furnace takes advantage of the temperature dependent solubility of re-
fractory materials in various fluxes. A cylindrical boule with a coni-
cally tapered base is filled from bottom to top with a seed crystal,
a layer of flux, and a dense column of feed (oxide) material. The whole
boule is heated up to just below the melting point of the flux, then a
hot ring placed exactly at the level of the flux layer heats this thin
zone of the boule to a higher temperature so as to melt the flux. The
boule is then dropped slowly (e.g., <1 cm/day) down through the hot ring.
The molten layer of flux dissolves the feed material above and deposits
a single crystal below.

The basic components of the furnace are the frame, the heating
column, the clock drive, and the power supplies. The frame is a simple

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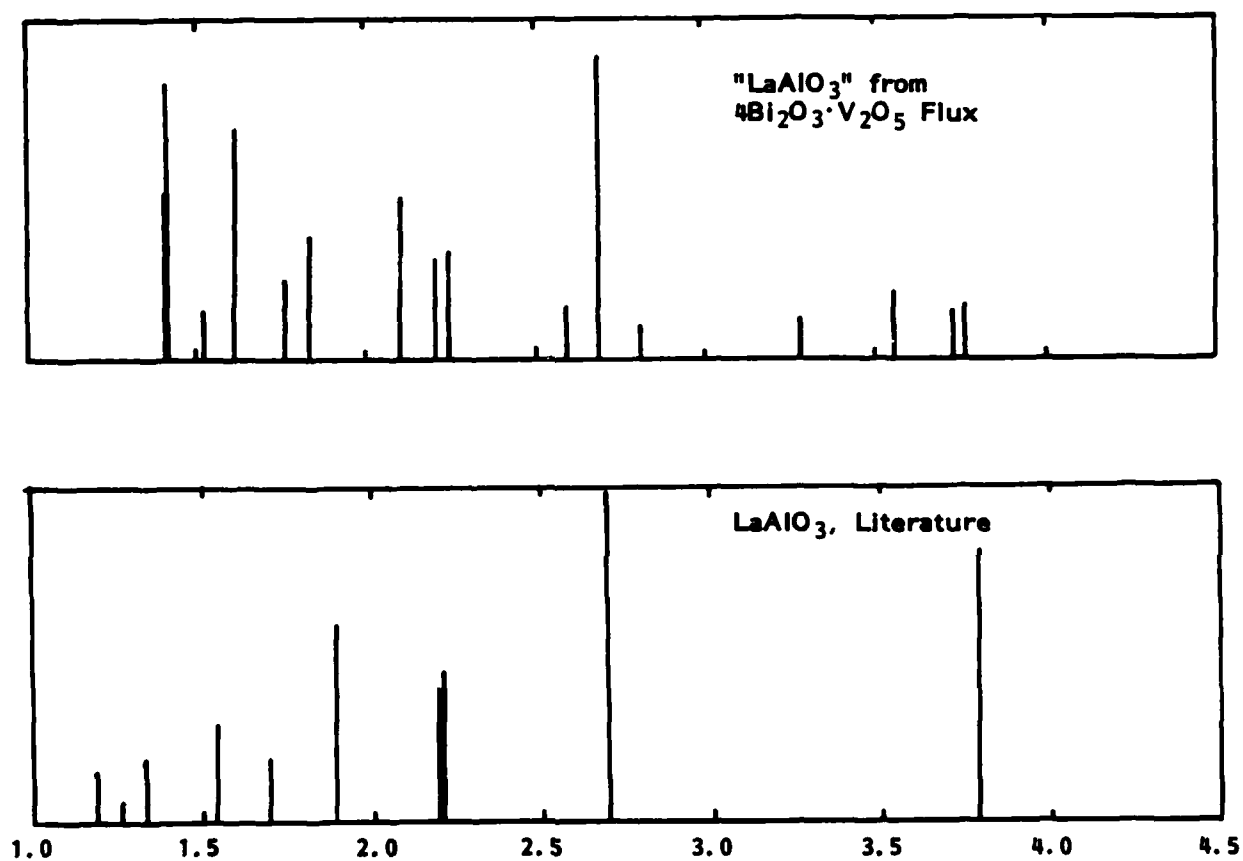
Figure 3. X-ray spectrum of product of reaction of 1:1 La_2O_3, Al_2O_3 (1% Ce_2O_3) carried out in a flux of $4Bi_2O_3 \cdot V_2O_5$.

LaAlO$_3$ from KF

LaAl$_{0.7}$Sc$_{0.3}$O$_3$ from KF

La$_3$Sc$_2$Ga$_3$O$_{12}$ Garnet
(Literature)

1.0   1.5   2.0   2.5   3.0   3.5   4.0   4.5
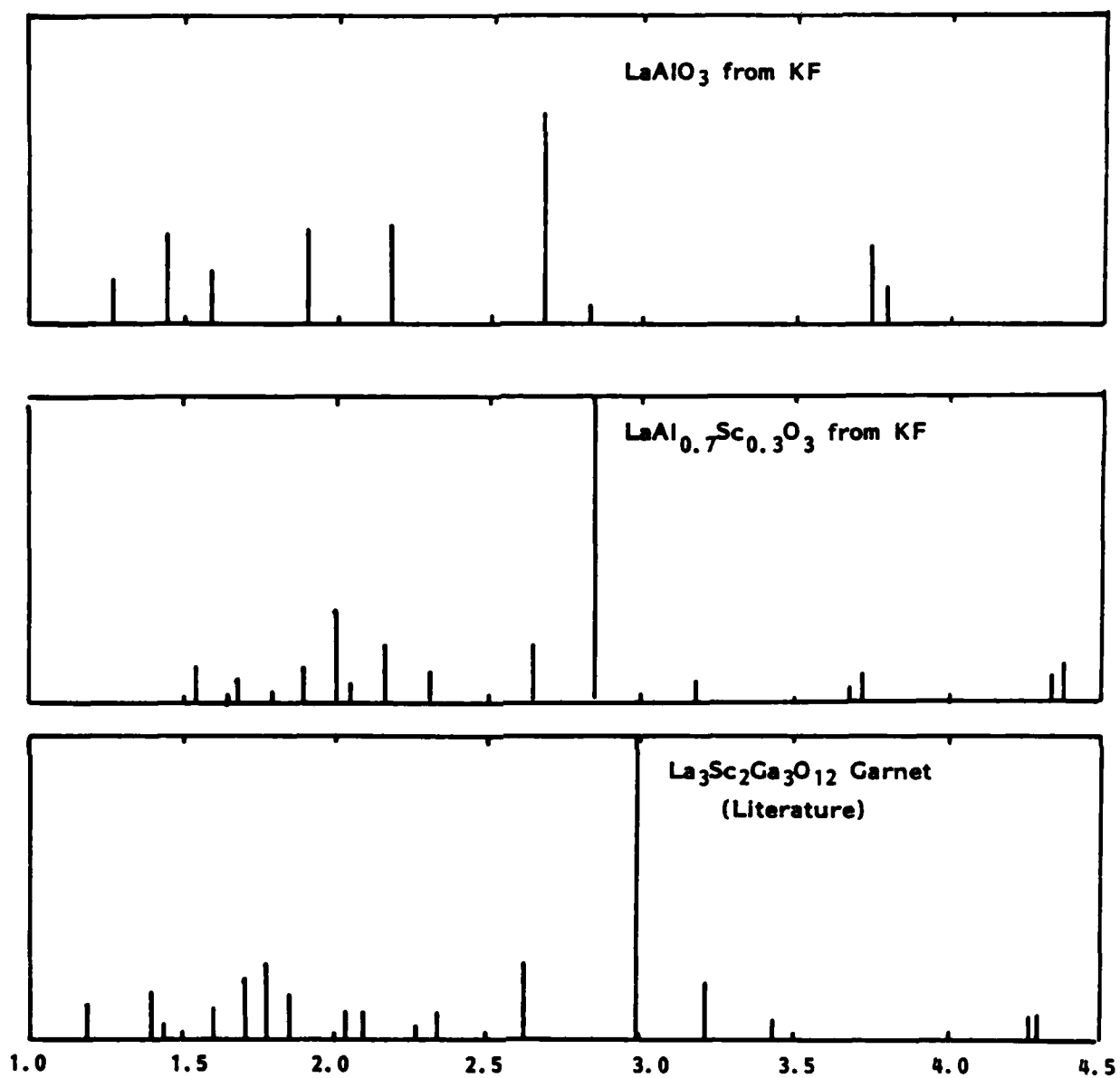
Figure 4. X-ray spectra of products of La oxide syntheses conducted in molten KF flux.

13" x 24" x 24" angle-iron assembly with plenty of holes and crossbars for attaching parts. The other components are described in detail.

The heating column is a three-zone tube furnace. The identical outer zones consist of Kanthal REH B 7-30 tube elements wrapped in a 2" blanket of Kaowool ceramic insulation and secured by ring clamps (see photograph, Figure 5). The middle zone is a 1" diameter Kanthal K 3/6 "Superelement," a thin $MoSi_2$ ring capable of attaining temperatures in excess of 1500°C. This element was fitted with a ceramic retaining block which served multiple functions: 1) to retain and position the fragile ring element; 2) to expose only a narrow slit of the ring element to the furnace center; 3) to position the outer zones of the furnace concentrically with each other and the ring. This last function was achieved by machining helical grooves into the holder which match the ends of the Kanthal tube elements. The retaining block material was a soft, low density refractory, Salir, manufactured by Zircar Corp. The ring element and retaining block are shown in the accompanying photographs (Figure 6).

Alumina tubes were passed through the Kanthal elements and positioned by a groove in the ring element retainer. These protect the boule from electrical hazards and thermal discontinuities presented by the Kanthal heating coils. A stainless steel adaptor was attached to the bottom of the column to allow passage of argon through the furnace.

Figure 7 is a drawing of the hot ring and retainer, the upper alumina tube, and the boule. The boule, shown in its loading position at the top of the furnace, is a vitreous carbon cylinder tapered to a point at the bottom to allow insertion of a seed crystal. A carriage made of stainless steel washers and oxidation resistant metal wires (e.g., W, Ni, or Mo) attach the boule to the clock-drive. The clock is a 1 or 1/12 rph motor with a gear train which allows selection of a variety of dropping rates in the range of 1 to 50 mm per day.

Figure 8 is a schematic of the power supply to the outer and center zones of the furnace. The Kanthal tube elements operate at a nominal 24V/58A, and were driven by high-current transformers powered by small, 10A variacs (20A variacs will be needed if the elements are to be operated near full power). The ring element requires a nominal 6V/40A and was powered by an externally programmable Sorenson SRL 40-50 DC power supply regulated by an LFE temperature controller. These instruments were compatible with no fuss, and excellent temperature regulation was achieved.

Temperature profiles of the furnace were obtained by dropping a thermocouple down the center tube and measuring temperature as a function of distance from the top of the furnace. The variables which determine the shape of this profile are the power applied to the outer zones, the temperature setting of the hot ring, and the rate of flow of argon or other gas through the furnace. It is expected that the presence of the boule in the furnace will radically alter the profile shape. It is

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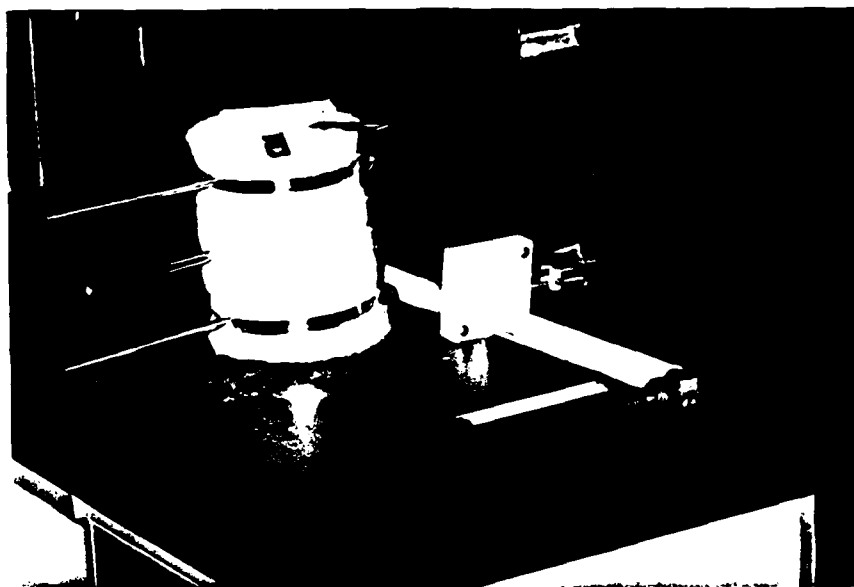
Figure 5. Photograph showing disassembled TSZ crystal growing furnace, including insulation wrapped 2-zone furnace and supports, the central ceramic guide tubes with inert atmosphere purge adaptor, and the central $MoSi_2$ ring heating element with ceramic retainer.
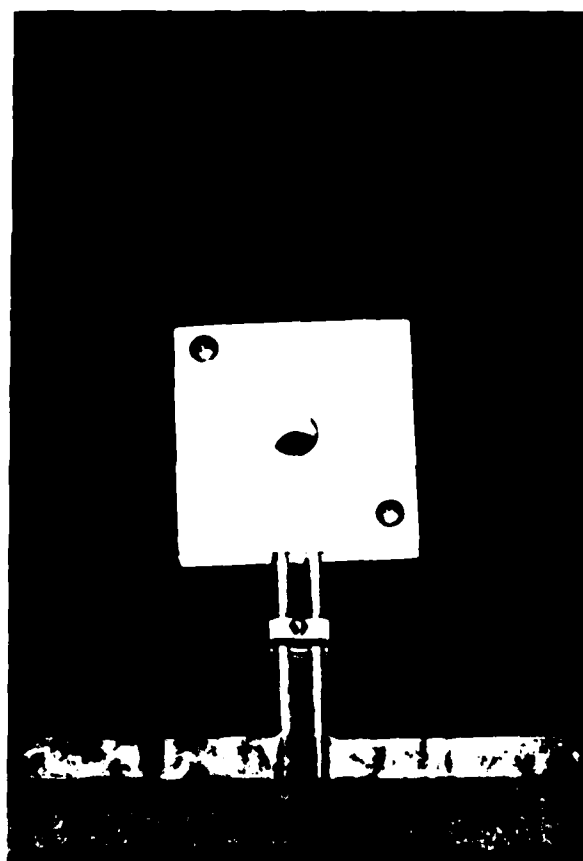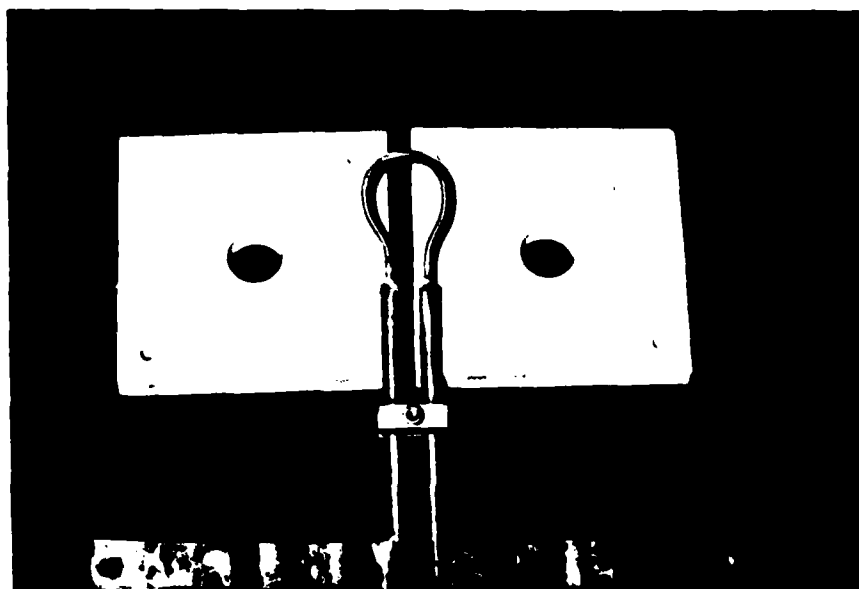
Figure 6. Mobiγ ring element and sensor retainer
f r h t one in TSC crystal m str tar-
n ter.
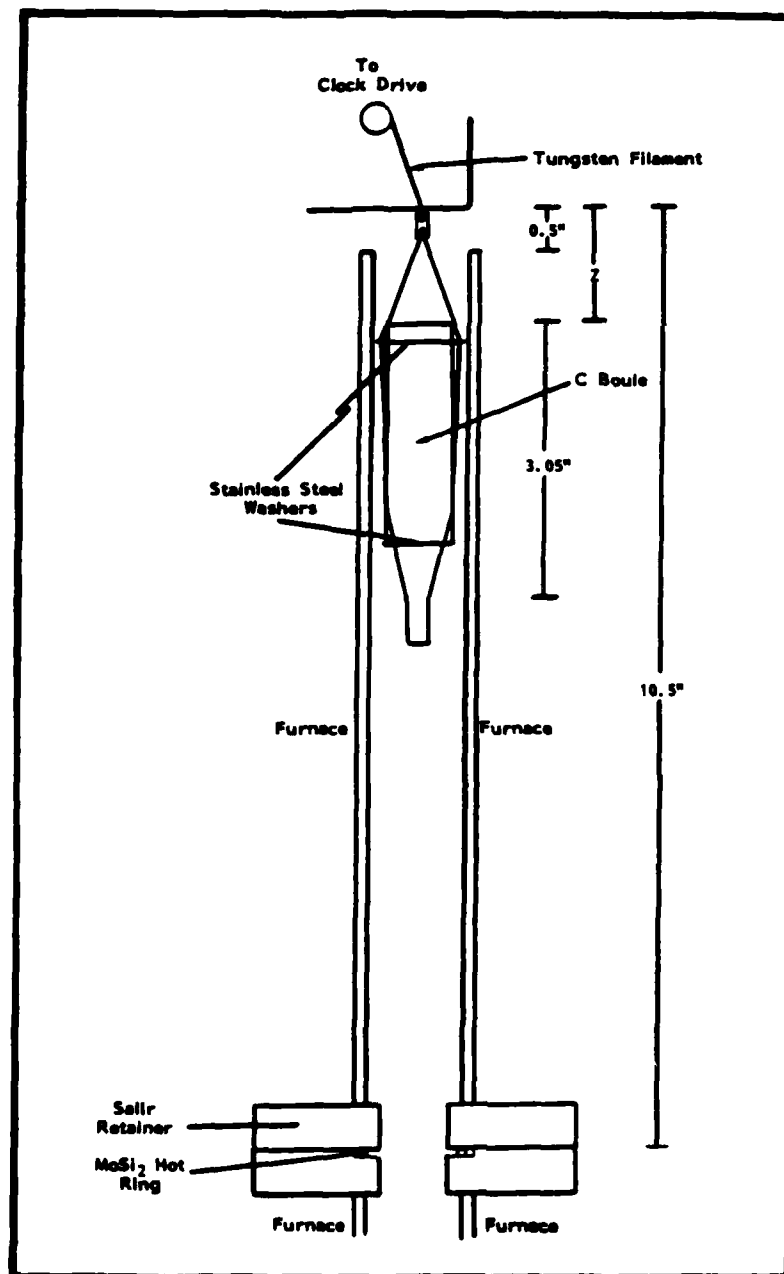
Figure 7. Boule, lowering mechanism and furnace interior for TSZ crystal growth.

17
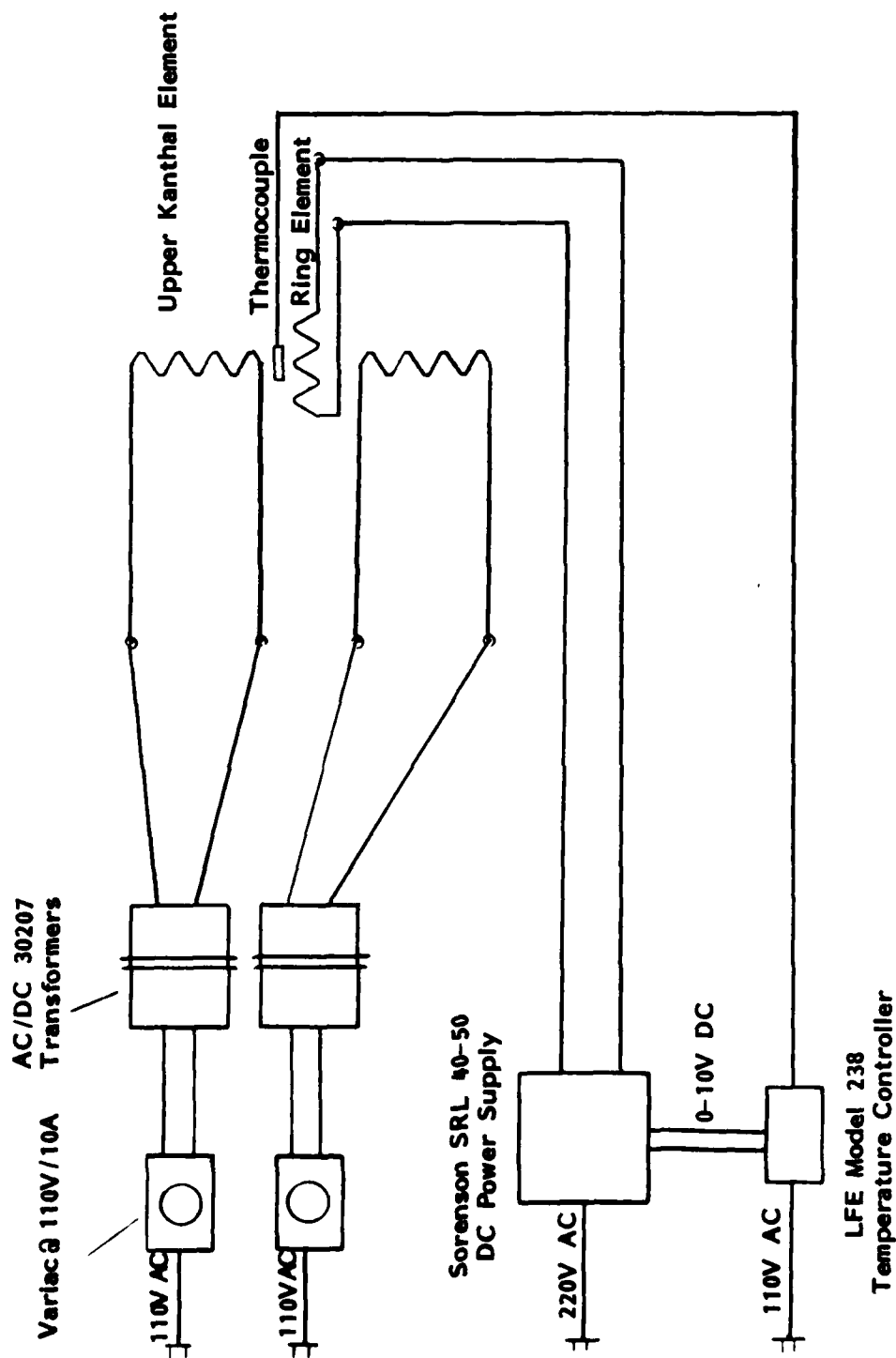
Figure 8. Wiring schematic for 3-zone traveling solvent zone furnace.

Upper Kanthal Element

Thermocouple

Ring Element

AC/DC 30207
Transformers

Variac 110V/10A

110V AC

110V AC

Sorenson SRL 40-50
DC Power Supply

0-10V DC

220V AC

110V AC

LFE Model 238
Temperature Controller

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desirable to have a sharply defined temperature peak, with the high temperature zone (i.e., the region over which T is sufficient to melt the flux) occurring over a vertical distance of <1 cm. Figure 9 depicts the best profile obtained to date from our furnace. Supposing we were using a potassium fluoride flux (mp. = 850°C), the high temperature zone occurs over a vertical distance of 1 inch. This profile was obtained with the outer-zone variacs set to 15V (and thoroughly equilibrated), the ring temperature at 1250°C, and no Ar flow.

2. <u>TSZ Flux Growth Experiments</u>. Several trial runs have been made in our furance. None of these runs were successful in producing single crystals.

The first series of runs used an open boule containing an $LaAlO_3$ oxide mix with 10 m/o KF flux. Very soon after turning on the hot ring, the Mo filament holding the boule gave, apparently having been corroded by flux vapor.

In the second trial, the KF flux was not mixed with the oxide, but was melted into a plug at the bottom of the boule. A platinum foil cap was wired to the top of the boule, and a tungsten filament replaced the molybdenum of run 1. Approximately 4 hours after turning on the hot ring, the boule fell to the bottom of the furnace. This time the boule itself had oxidized, indicating that measures must be taken to seal the furnace interior from the atmosphere. The material at the tip of the boule contained some small, nonluminescent crystals, <1 mm to an edge. These were analyzed as $LaAlO_3$ by X-ray diffraction. It soon became obvious that volatility of the fluoride flux was a major problem. Time permitted us only one attempted solution at operating the growth experiment in a closed system. In this experiment, a cylindrical nickel crucible containing a plug of KF flux, a stoichiometric ($LaAlO_3$) oxide mix, and capped with a nickel cap, was vacuum-sealed inside a quartz ampoule. This ampoule was then dropped down the furnace. Approximately 12 hours after turning on the hot ring, the ampoule exploded, apparently due to a buildup of internal pressure and a weakening of the quartz walls by fluoride vapor.

The furnace has been repaired and supplied with a fireproof ceramic base, and is ready for further use.
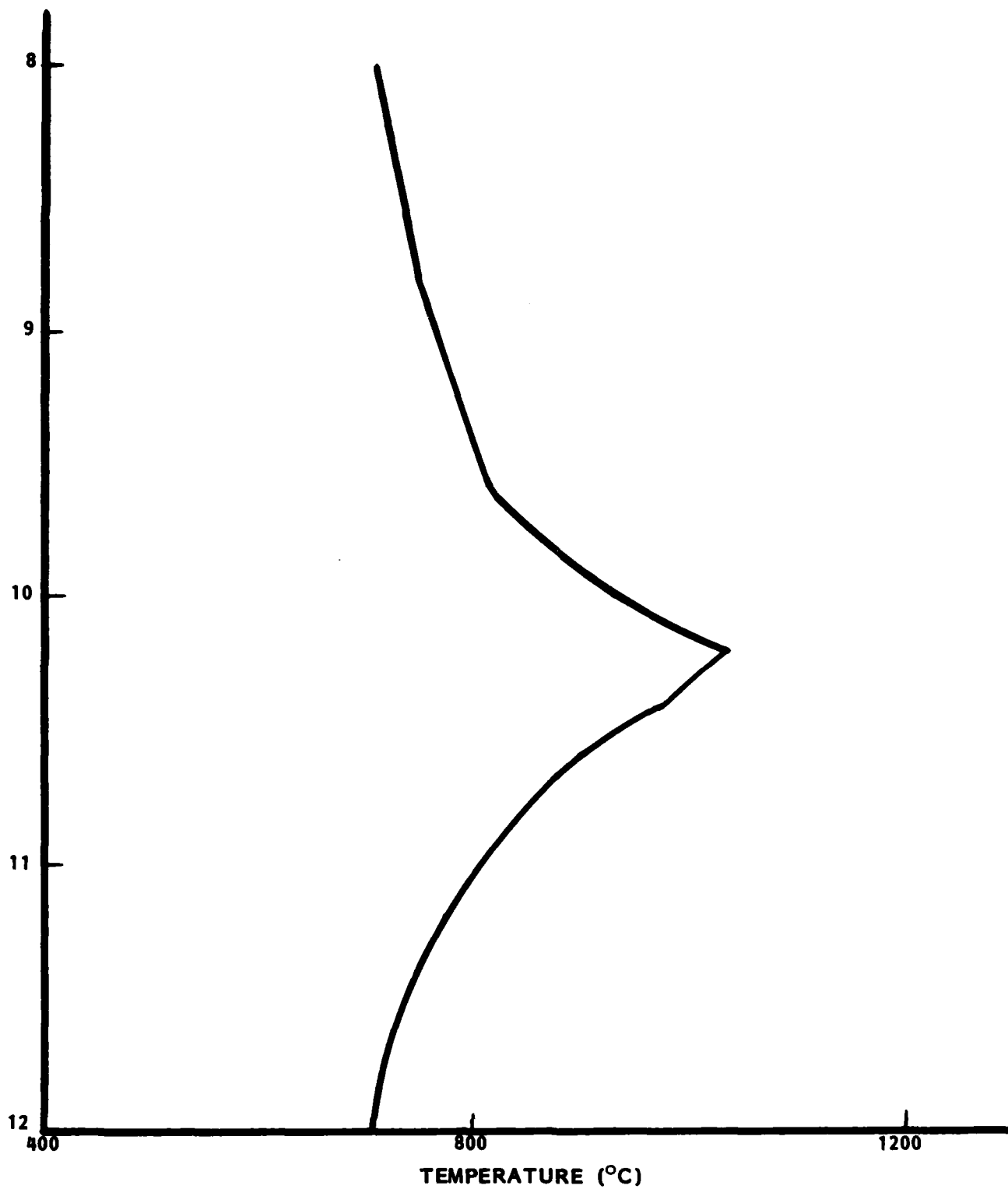
Figure 9. Typical temperature profile for crystal growth furnace.

CONCLUSIONS

Although the crystal growth experiments did not yield crystals suit-
able for optical evaluation, the compound synthesis, furnace construction,
and trial TSZ runs did provide a basis for further research. We draw the
following conclusions from these experiments:

- A single phase cubic mixed oxide of formula $LaAl_xSc_{1-x}O_3$
  can be produced by arc melting of stoichiometric mixtures
  of the component oxides. The lattice dimensions are
  expanded compared to $LaAlO_3$.

- Although synthesis of $LaAlO_3$ and $LaAl_{1-x}Sc_xO_3$ from oxide
  fluxes was unsuccessful here, it has been reported else-
  where.[15] However, oxidizing fluxes are not likely to be
  compatible with Ce_2O_3, which is easily oxidized itself.
  Hence, we chose to emphasize the neutral flux, KF, which
  has been used to grow other perovskites.

- $LaAlO_3$ was produced successfully in KF between 1250 and
  750°C. The mixed $LaAl_{1-x}Sc_xO_3$ may have produced a garnet
  phase, which in itself would be a candidate cubic crystal
  host for Ce^{+3}.

- The only luminescent Ce-doped oxides produced so far in
  this laboratory have employed CeF_3 as a dopant source.
  It may be that Ce_2O_3, which cannot be obtained in high
  purity, is so sensitive to oxidation that, even under
  neutral conditions, residual oxygen in the growth appa-
  ratus is sufficient to convert it to CeO_2.

- The failure of the TSZ growth was due to KF flux vola-
  tility and reactivity, as well as apparent air leaks
  into the growth chamber. We would make the following
  modifications to the growth apparatus in order to prevent
  malfunction:

  1) The charge should be hermetically sealed in a KF-
     resistant thin walled boule, e.g., Pt or perhaps
     Ni or Zr. This could be done in an arc welder
     under inert atmosphere.

---

[15]T. Takeda, T. Miyata, F. Muramatsu and T. Tomiki, J. Electrochem.
Soc. 127, 438 (1980).

2) The boule should be sealed into an evacuated quartz tube to eliminate the necessity of making the growth furnace absolutely airtight.

3) The use of rf heating of the hot zone should be consistent, since the thermally heated zone had a rather broad temperature profile.

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APPENDIX

During this program we have begun an examination of the theoretical basis for interpretation of Ce^{+3} luminescence in various hosts. We note that green luminescence has been well documented for Ce in yttrium alumina garnet, where $O^=$ coordination is eightfold cubic. In addition, blue-green luminescence of Ce^{+3} appears to have been observed in the cubic perovskite hosts $LaAlO_3$ and $LaAl_xSc_{1-x}O_3$, with a dodecahedral $O^=$ coordination in the cubic "A" site of ABO_3 lattice. However, the emission spectrum of Ce^{+3} in the perovskite $YAlO_3$ is in the ultraviolet spectral region ($\lambda_{max} \approx 360$ nm). $YAlO_3$ has a distorted perovskite structure, or D_2h symmetry, similar to $GdFeO_3$ (Figure 4), while $LaAlO_3$ is nearly cubic. Thus, the Ce^{+3} fluorescence energy appears to be very sensitive to rather small changes in the crystalline environment.

It would be valuable to have a ready means of predicting the effects of hot lattice parameters and geometry on Ce^{+3} energy levels, as an aid to interpretation of luminescence and absorption spectra. To this end, we have written a simple crystal field program for use with the IBM personal computer with 128K of memory. The program is written in the IBM Fortran language, and is thus easily modified to run on larger IBM computers. It is reproduced at the end of this appendix, and is fully documented so as to be self-explanatory. A copy of the disk is available from EIC Laboratories.

In operating the program on a standard IBM PC, the calculation can be quite slow. A small change in the calculation of the matrix elements translates to a larger change in the resultant eigenvalues. The consequence of this is that in order to calculate the energy levels to within ~10%, the matrix elements must be computed to <1% accuracy. A Monte Carlo technique is used to compute the numerical values of the integrals. Our benchmark tests of the program indicate that in order to achieve such precision, a total of 1.5×10^6 Monte Carlo steps are required for tenfold coordination. Other integration algorithms may be possible, but this is obviously the "rate determining step." A recent development which can be used with the IBM PC is the INTEL 8087 coprocessor chip for high speed floating point numerical operations. This device should be capable of enhancing the speed of the integration by more than a factor of 10.

24

```
      cat eic.f
C
C------------------------------------------------------------------
C
C             CRYSTAL FIELD CALCULATION FOR CE+3 ION
C
C------------------------------------------------------------------
C
C
C    PURPOSE:THIS PROGRAM PERFORMS DEGENERATE PERTURBATION THEORY
C            CALCULATIONS FOR THE 5-D LEVELS OF ANY ION IN THE
C            ELECTROSTATIC FIELD OF OF ANY OTHER IONS. THE POTENTIAL
C            OF INTERACTION MUST BE SUPPLIED IN AN FUNCTION POT(X,Y,Z)
C            THIS POTENTIAL FUNCTION CAN BE COMPILED SEPARATELY AND
C            LINKED TO THE OBJECT CODE OF THIS PROGRAM USING THE IBM
C            LINKER. THE POTENTIAL FUNCTION MUST BE EXPANDED IN A
C            TAYLOR-SERIES AS DESCRIBED IN TINKHAMS BOOK 'GROUP
C            THEORY AND QUANTUM MECHANICS ' PS 68. ONLY THE FIRST
C            TERM WITH NONSPHERICAL SYMMETRY NEED BE KEPT.
C
C------------------------------------------------------------------
C
C    METHOD: THE PROGRAMS OPERATES IN THE FOLLOWING SEQUENCE. FIRST
C            THE COMPUTATION PARAMETERS ARE ESTABLISHED. THE NEXT
C            STEP IS TO COMPUTE THE MATRIX ELEMTENTS <5DIVI5D>.
C            SINCE THE MATRIX IS BOTH REAL AND SYMMETRIC, ONLY 15
C            MATRIX ELEMENTS ARE COMPUTED. THE 3-DIMENSIONAL
C            INTEGRALS ARE COMPUTED USING A MONTE-CARLO INTEGRATION
C            METHOD. TO ACHEIVE AN ACCURACY OF 5% APPROXIMATELY
C            5000 POINTS ARE REQUIRED. THE RANDOM NUMBERS ARE READ
C            INTO THE ARRAYS X,Y,Z. THIS WAS DONE TO IMPROVE THE
C            SPEED OF THE CALCULATION.THE FINAL STEP IS TO COMPUTE
C            THE EIGENVALUES. THE SUBROUTINE EIGEN ACCOMPLISHES THIS
C            USING THE DIAGONALIZATION METHOD ORIGINATED BY
C            JACOBI AND ADAPTED BY VON NEUMANN FOR LARGE COMPUTERS.
C
C------------------------------------------------------------------
C
C    USAGE: THE FOLLOWING SUBROUTINES ARE USED
C           EIGEN: COMPUTES EIGENVALUES OF A REAL SYMMETRIC MATRIX
C           INTEG: MONTE-CARLO INTEGRATION ROUTINE
C           CHANG:CONVERTS MATRIX M TO STORAGE MODE=1 MATRIX A
C
C           THE FOLLOWING FUNCTION ARE USED
C           F5DXY,F5DYZ,F5DZX,F5DZ2,F5D22
C           G5DXY,G5DYZ,G5DZX,G5DZ2,G5D22
C
C
C------------------------------------------------------------------
C
C REQUIREMENTS: AN ADDITIONAL FUNCTION POT(X,Y,Z) MUST BE SUPPLIED
C               SEE DOCUMENTATION FOR DETAILS.
C
C------------------------------------------------------------------
```

```
C
C   MAIN PROGRAM
C
$STORAGE:2
      PROGRAM CRYST
      EXTERNAL F5DXY,F5DYZ,F5DZX,F5DZ2,F5D22
      EXTERNAL G5DXY,G5DYZ,G5DZX,G5DZ2,G5D22
      REAL*4 M(5,5),A(15),R(15)
      COMMON /RNDDAT/ X(5000),Y(5000),Z(5000)
      COMMON /PARAM/ZE,ZO,BD
C
C   INPUT CALCULATION PARAMETERS
C
   5  WRITE(*,10)
  10  FORMAT(' ENTER 0 TO RUN WITH INTERNAL PARAMETERS')
C INTERNAL PARAMETERS ARE:
C                          CHARGE ON CE+=2.0
C                          CHARGE ON O =-2.0
C                          LATTICE PARAMETER=2.0 BOHRS
      WRITE(*,20)
  20  FORMAT(' ENTER 1 TO SPECIFY NEW PARAMETERS')
      READ(*,30)ICHOIC
  30  FORMAT(I1)
      IF(ICHOIC.EQ.1)GOTO 40
      IF(ICHOIC.NE.0)GOTO 5
      BD=2.0
      ZE=2.0
      ZO=2.0
      GOTO 99
  40  WRITE(*,50)
  50  FORMAT(' INPUT EFFECTIVE NUCLEAR CHARGE F4.2')
      READ(*,60)ZE
  60  FORMAT(F4.2)
      WRITE(*,70)
  70  FORMAT(' INPUT CHARGE ON OXYGEN F4.2')
      READ(*,80)ZO
  80  FORMAT(F4.2)
      WRITE(*,90)
  90  FORMAT(' LATTICE PARAMETER F4.2')
      READ(*,100)BD
 100  FORMAT(F4.2)
  99  CONTINUE
C
C   COMPUTE MATRIX ELEMENTS
C
      WRITE(*,23)
  23  FORMAT(' HOW MANY MONTE-CARLO POINTS (I4) LESS THAN 5000')
      READ(*,24)NSTEP
  24  FORMAT(I4)
      WRITE(*,333)
 333  FORMAT(' READING IN MONTE-CARLO DATA')
      OPEN(1,FILE='RANDOM')
```

```fortran
C READ IN THE RANDOM NUMBERS AND SCALE THEM TO SPAN -20 TO +20
      DO 444 I=1,NSTEP
      READ(1,555)X(I),Y(I),Z(I)
      X(I)=X(I)*40.0-20.0
      Y(I)=Y(I)*40.0-20.0
      Z(I)=Z(I)*40.0-20.0
 555  FORMAT(3F8.7)
 444  CONTINUE
      CLOSE(1,STATUS='KEEP')
      OPEN(2,FILE='RESULTS')
C
C  COMPUTE MATRIX ELEMENTS
C  EACH CALL OF INTEG COMPUTES ONE MATRIX ELEMENT
C
      WRITE(*,158)
      CALL INTEG(F5DXY,G5DXY,M(1,1),NSTEP)
      WRITE(*,158)
      CALL INTEG(F5DXY,F5DYZ,M(1,2),NSTEP)
      WRITE(*,158)
      CALL INTEG(F5DYZ,G5DYZ,M(2,2),NSTEP)
      WRITE(*,158)
      CALL INTEG(F5DXY,F5DZX,M(1,3),NSTEP)
      WRITE(*,158)
      CALL INTEG(F5DYZ,F5DZX,M(2,3),NSTEP)
      WRITE(*,158)
      CALL INTEG(F5DZX,G5DZX,M(3,3),NSTEP)
      WRITE(*,158)
      CALL INTEG(F5DXY,F5DZ2,M(1,4),NSTEP)
      WRITE(*,158)
      CALL INTEG(F5DYZ,F5DZ2,M(2,4),NSTEP)
      WRITE(*,158)
      CALL INTEG(F5DZX,F5DZ2,M(3,4),NSTEP)
      WRITE(*,158)
      CALL INTEG(F5DZ2,G5DZ2,M(4,4),NSTEP)
      WRITE(*,158)
      CALL INTEG(F5DXY,F5D22,M(1,5),NSTEP)
      WRITE(*,158)
      CALL INTEG(F5DYZ,F5D22,M(2,5),NSTEP)
      WRITE(*,158)
      CALL INTEG(F5DZX,F5D22,M(3,5),NSTEP)
      WRITE(*,158)
      CALL INTEG(F5DZ2,F5D22,M(4,5),NSTEP)
      WRITE(*,158)
      CALL INTEG(F5D22,G5D22,M(5,5),NSTEP)
 158  FORMAT(' COMPUTING MATRIX ELEMENT')
C
C  SYMMETIZE MATRIX M
C
      DO 150 J=1,5
      DO 150 I=1,J
 150  M(J,I)=M(I,J)
C
C     COMPUTE EIGENVALUES
C
```

```
      WRITE(*,159)
  159 FORMAT(' COMPUTING EIGENVALUES')
      N=5
      MV=1
C  FIRST CONVERTS MATRIX M TO STORAGE MODE 1 MATRIX A
      CALL CHANG(M,A)
      CALL EIGEN(A,R,N,MV)
C
      WRITE(*,63)
      WRITE(2,63)
   63 FORMAT(' THE CALCULATION PARAMETERS ARE.....')
      WRITE(*,64)ZO
      WRITE(2,64)ZO
   64 FORMAT(/' CHARGE ON OXYGEN  ',F4.2)
      WRITE(*,65)ZE
      WRITE(2,65)ZE
   65 FORMAT(' EFFECTIVE NUCLEAR CHARGE  ',F4.2)
      WRITE(*,66)BD
      WRITE(2,66)BD
   66 FORMAT(' LATTICE PARAMETER  ',F4.2)
      WRITE(*,201)
      WRITE(2,201)
  201 FORMAT(' THE EIGENVALUES ARE.....')
      WRITE(*,645)A(1),A(3),A(6),A(10),A(15)
      WRITE(2,645)A(1),A(3),A(6),A(10),A(15)
  645 FORMAT(5E14.6)
      CLOSE(2,STATUS='KEEP')
      END
C
C INTEGRATION SUBROUTINE
C
C  THIS SUBROUTINE COMPUTES THE 3-D INTEGRAL OF F1*POT*F2
C  WHERE F1 AND F2 ARE EXTERNAL FUNCTIONS REPRESENTING THE
C  ANY TWO OF THE 5D ORBITALS AND POT IS THE POTENTIAL
C  DUE TO THE COORDINATED OXYGEN IONS.
C  THE INTEGRATION METHOD IS MONTE-CARLO. THE RANDOM NUMBERS
C  ARE STORED IN THE ARRAYS X,Y,Z
C
      SUBROUTINE INTEG(F1,F2,VALU,NSTEP)
      EXTERNAL F1,F2
      COMMON /RNDDAT/ X(5000),Y(5000),Z(5000)
      COMMON /PARAM/ZE,ZO,BD
      CONST=SQRT(3.00)/1536.0/SQRT(3.14159265)
      CONST=CONST*ZE**3.5
      VALU=0.0
      RANGE=40.0
      DO 20 I=1,NSTEP
      VALU=VALU+F1(X(I),Y(I),Z(I),ZE)*F2(X(I),Y(I),Z(I),ZE)
     9*POT(X(I),Y(I),Z(I))
   20 CONTINUE
      VALU=VALU*CONST*CONST*40.00/FLOAT(NSTEP)
      WRITE(*,245)VALU
      WRITE(2,245)VALU
  245 FORMAT(E14.6)
      END
```

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```
      SUBROUTINE CHANG(M,A)
C CONVERT THE MATRIX M TO MATRIX A (STORAGE MODE=1) FOR USE
C BY EIGEN.
      REAL*4 M(5,5),A(15)
      K=1
      DO 10 J=1,5
      DO 10 I=1,J
      A(K)=M(I,J)
  10  K=K+1
      END
C
C    5D ORBITAL FUNCTIONS
C
C 5DXY ORBITAL
      FUNCTION F5DXY(X,Y,Z,ZE)
      R2=X*X+Y*Y+Z*Z
      R=SQRT(R2)
      F5DXY=(6.0-ZE*R/2.0)*2.0*X*Y*EXP(-1.0*ZE*R/4.0)
      END
C 5DYZ ORBITAL
      FUNCTION F5DYZ(X,Y,Z,ZE)
      R2=X*X+Y*Y+Z*Z
      R=SQRT(R2)
      F5DYZ=(6.0-ZE*R/2.0)*2.0*Y*Z*EXP(-1.0*ZE*R/4.0)
      END
C 5DZX ORBITAL
      FUNCTION F5DZX(X,Y,Z,ZE)
      R2=X*X+Y*Y+Z*Z
      R=SQRT(R2)
      F5DZX=(6.0-ZE*R/2.0)*2.0*Z*X*EXP(-1.0*ZE*R/4.0)
      END
C 5DZ*Z ORBITAL
      FUNCTION F5DZ2(X,Y,Z,ZE)
      R2=X*X+Y*Y+Z*Z
      R=SQRT(R2)
      T=(3.0*Z*Z-R2)*(6.0-ZE*R/2.0)/SQRT(3.0)
      F5DZ2=T*EXP(-1.0*ZE*R/4.0)
      END
C 5DX*X-Y*Y ORBITAL
      FUNCTION F5D22(X,Y,Z,ZE)
      R2=X*X+Y*Y+Z*Z
      R=SQRT(R2)
      T=(X*X-Y*Y)*(6.0-ZE*R/2.00)
      F5D22=T*EXP(-1.0*ZE*R/4.0)
      END
C 5DXY ORBITAL
      FUNCTION G5DXY(X,Y,Z,ZE)
      R2=X*X+Y*Y+Z*Z
      R=SQRT(R2)
      G5DXY=(6.0-ZE*R/2.0)*2.0*X*Y*EXP(-1.0*ZE*R/4.0)
      END
```

```
C 5DYZ ORBITAL
      FUNCTION G5DYZ(X,Y,Z,ZE)
      R2=X*X+Y*Y+Z*Z
      R=SQRT(R2)
      G5DYZ=(6.0-ZE*R/2.0)*2.0*Y*Z*EXP(-1.0*ZE*R/4.0)
      END
C 5DZX ORBITAL
      FUNTION G5DZX(X,Y,Z,ZE)
      R2=X*X+Y*Y+Z*Z
      R=SQRT(R2)

C      R=SQRT(R2)
      T=(3.0*Z*Z-R2)*(6.0-ZE*R/2.0)/SQRT(3.0)
      G5DZ2=T*EXP(-1.0*ZE*R/4.0)
      END
C 5DX*X-Y*Y ORBITAL
      FUNCTION G5D22(X,Y,Z,ZE)
      R2=X*X+Y*Y+Z*Z
      R=SQRT(R2)
      T=(X*X-Y*Y)*(6.0-ZE*R/2.00)
      G5D22=T*EXP(-1.0*ZE*R/4.0)
      END
C
C-------------------------------------------------------------------
C
C          SUBROUTINE EIGEN
C
C          PURPOSE
C              COMPUTE EIGENVALUES AND EIGENVECTORS OF A REAL SYMMETRIC
C              MATRIX
C
C          USAGE
C              CALL EIGEN(A,R,N,MV)
C
C          DESCRIPTION OF PARAMETERS
C              A - ORIGINAL MATRIX (SYMMETRIC), DESTROYED IN COMPUTATION.
C                  RESULTANT EIGENVALUES ARE DEVELOPED IN DIAGONAL OF
C                  MATRIX A IN DESCENDING ORDER.
C              R - RESULTANT MATRIX OF EIGENVECTORS (STORED COLUMNWISE,
C                  IN SAME SEQUENCE AS EIGENVALUES)
C              N - ORDER OF MATRICES A AND R
C              MV- INPUT CODE
C                      0    COMPUTE EIGENVALUES AND EIGENVECTORS
C                      1    COMPUTE EIGENVALUES ONLY (R NEED NOT BE
C                           DIMENSIONED BUT MUST STILL APPEAR IN CALLING
C                           SEQUENCE)
C
C          REMARKS
C              ORIGINAL MATRIX A MUST BE REAL SYMMETRIC (STORAGE MODE=1)
C              MATRIX A CANNOT BE IN THE SAME LOCATION AS MATRIX R
C
C          SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C              NONE
```

```
C          METHOD
C              DIAGONALIZATION METHOD ORIGINATED BY JACOBI AND ADAPTED
C              BY VON NEUMANN FOR LARGE COMPUTERS AS FOUND IN 'MATHEMATICA
C              METHODS FOR DIGITAL COMPUTERS', EDITED BY A. RALSTON AND
C              H.S. WILF, JOHN WILEY AND SONS, NEW YORK, 1962, CHAPTER 7
C
C-----------------------------------------------------------------------
C
      SUBROUTINE EIGEN(A,R,N,MV)
      REAL*4 A(15),R(15)
C
C-----------------------------------------------------------------------
C
C
C          IF A DOUBLE PRECISION VERSION OF THIS ROUTINE IS DESIRED, THE
C          C IN COLUMN 1 SHOULD BE REMOVED FROM THE DOUBLE PRECISION
C          STATEMENT WHICH FOLLOWS.
C
C     DOUBLE PRECISION A,R,ANORM,ANRMX,THR,X,Y,SINX,SINX2,COSX,
C    1                 COSX2,SINCS,RANGE,DSQRT,DABS
C
C          THE C MUST ALSO BE REMOVED FROM DOUBLE PRECISION STATEMENTS
C          APPEARING IN OTHER ROUTINES USED IN CONJUNCTION WITH THIS
C          ROUTINE.
C
C          THE DOUBLE PRECISION VERSION OF THIS SUBROUTINE MUST ALSO
C          CONTAIN DOUBLE PRECISION FORTRAN FUNCTIONS. SQRT IN STATEMENTS
C          40, 68, 75, AND 78 MUST BE CHANGED TO DSQRT.  ABS IN STATEMENT
C          62 MUST BE CHANGED TO DABS. THE CONSTANT IN STATEMENT 5 SHOULD
C          BE CHANGED TO 1.0D-12.
C
C-----------------------------------------------------------------------
C
C
C          GENERATE IDENTITY MATRIX
C
    5 RANGE=1.0E-6
      IF(MV-1) 10,25,10
   10 IQ=-N
      DO 20 J=1,N
      IQ=IQ+N
      DO 20 I=1,N
      IJ=IQ+I
      R(IJ)=0.0
      IF(I-J) 20,15,20
   15 R(IJ)=1.0
   20 CONTINUE
C
C          COMPUTE INITIAL AND FINAL NORMS (ANORM AND ANORMX)
C
   25 ANORM=0.0
      DO 35 I=1,N
      DO 35 J=I,N
      IF(I-J) 30,35,30
   30 IA=I+(J*J-J)/2
      ANORM=ANORM+A(IA)*A(IA)
   35 CONTINUE
      IF(ANORM) 165,165,40
   40 ANORM=1.414*SQRT(ANORM)
      ANRMX=ANORM*RANGE/FLOAT(N)
```

31

```
C              INITIALIZE INDICATORS AND COMPUTE THRESHOLD, THR
C
       IND=0
       THR=ANORM
    45 THR=THR/FLOAT(N)
    50 L=1
    55 M=L+1
C
C          COMPUTE SIN AND COS
C
    60 MQ=(M*M-M)/2
       LQ=(L*L-L)/2
       LM=L+MQ
    62 IF( ABS(A(LM))-THR) 130,65,65
    65 IND=1
       LL=L+LQ
       MM=M+MQ
       X=0.5*(A(LL)-A(MM))
    68 Y=-A(LM)/ SQRT(A(LM)*A(LM)+X*X)
       IF(X) 70,75,75
    70 Y=-Y
    75 SINX=Y/ SQRT(2.0*(1.0+( SQRT(1.0-Y*Y))))
       SINX2=SINX*SINX
    78 COSX= SQRT(1.0-SINX2)
       COSX2=COSX*COSX
       SINCS =SINX*COSX
C
C          ROTATE L AND M COLUMNS
C
       ILQ=N*(L-1)
       IMQ=N*(M-1)
       DO 125 I=1,N
       IQ=(I*I-I)/2
       IF(I-L) 80,115,80
    80 IF(I-M) 85,115,90
    85 IM=I+MQ
       GO TO 95
    90 IM=M+IQ
    95 IF(I-L) 100,105,105
   100 IL=I+LQ
       GO TO 110
   105 IL=L+IQ
   110 X=A(IL)*COSX-A(IM)*SINX
       A(IM)=A(IL)*SINX+A(IM)*COSX
       A(IL)=X
   115 IF(MV-1) 120,125,120
   120 ILR=ILQ+I
       IMR=IMQ+I
       X=R(ILR)*COSX-R(IMR)*SINX
       R(IMR)=R(ILR)*SINX+R(IMR)*COSX
       R(ILR)=X
   125 CONTINUE
       X=2.0*A(LM)*SINCS
       Y=A(LL)*COSX2+A(MM)*SINX2-X
       X=A(LL)*SINX2+A(MM)*COSX2+X
       A(LM)=(A(LL)-A(MM))*SINCS+A(LM)*(COSX2-SINX2)
       A(LL)=Y
       A(MM)=X
```

```
C           TESTS FOR COMPLETION
C
C           TEST FOR M = LAST COLUMN
C
  130 IF(M-N) 135,140,135
  135 M=M+1
      GO TO 60
C
C           TEST FOR L = SECOND FROM LAST COLUMN
C
  140 IF(L-(N-1)) 145,150,145
  145 L=L+1
      GO TO 55
  150 IF(IND-1) 160,155,160
  155 IND=0
      GO TO 50
C
C           COMPARE THRESHOLD WITH FINAL NORM
C
  160 IF(THR-ANRMX) 165,165,45
C
C           SORT EIGENVALUES AND EIGENVECTORS
C
  165 IQ=-N
      DO 185 I=1,N
      IQ=IQ+N
      LL=I+(I*I-I)/2
      JQ=N*(I-2)
      DO 185 J=I,N
      JQ=JQ+N
      MM=J+(J*J-J)/2
      IF(A(LL)-A(MM)) 170,185,185
  170 X=A(LL)
      A(LL)=A(MM)
      A(MM)=X
      IF(MV-1) 175,185,175
  175 DO 180 K=1,N
      ILR=IQ+K
      IMR=JQ+K
      X=R(ILR)
      R(ILR)=R(IMR)
  180 R(IMR)=X
  185 CONTINUE
      END
%
```

HOW TO DESIGN A NEW POTENTIAL

The potential function used in this program is stored
in the file POT.FOR. This particular function applies only
to system with cubic symmetry. It must be modified for
performing calculations on other symmetry groups, but it
will work for the octahedral case as well as the 8 or 12
fold cubic cases. The reason for this is that the lowest
order non spherical term in the potential due to an octahedral
coordination of ions is the same as the cubic crystal field.

To determine what the appropriate potential function for
a particular problem is consider the following example.
Suppose we have an ion at the position x=-a,y=0,z=0.This ion
will contribute to the potential a term

$$V(x,y,z)=e[(a+x)**2+y**2+z**2]**-1/2$$

which can be expanded in a Taylor series to give

$$V(x,y,z)=e/a(1-x/a-r**2/2a**2+3/2*x**2/a**2+...)$$

If we place additional charges at the positions required
to form an octahedral coordination we find that a lot of
cancellation will occur. The first term with nonspherical symmetry
is

$$V(x,y,z)=35e/(4a**5)*(x**4+y**4+z**4-3/5*r**4)$$

By terms with spherical symmetry we mean terms like

$$V(x,y,z)=x**2+y**2+z**2$$

or powers of this.

This sort of Taylor series expansion of the potential
is necessary in crystal field calculations. Using the full
potential will not give the relevant splitting.

In order to study a particular distortion or other
symmetry group the first step is to determine the symmetry
group. A useful reference is Tinkham's book "Group Theory
and Quantum Mechanics" .

Once you have the potential function in it's Taylor series form
the next step is to write a short program in Fortran to use
with the other program. The program POT.FOR on this diskette
should serve as a model. To get a copy of it type in
TYPE POT.FOR.

The next step is to compile this program. The instructions
in the fortran manual should be consulted if the following directions
are not helpful.
1) type in FORMAT B:
2) insert a new diskette into the right hand disk drive
3) type in COPY A:CRYSTAL.OBJ B:
        this will copy the object code for the main
        program onto the new diskette

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4) type in COPY A:ED.COM B:
       this will copy the editor
5) type in COPY A:POT.FOR B:
       this copies the potential function
6) type in B:ED B:POT.FOR
       this allows you to edit the program
       refer to the DOS manual for using the editor
7) once you have edited your program remove this diskette from
8) from the left drive and insert the disk labelled FOR1
9) type in B:
10) type in A:FOR1
11) when the compiler ask you for the name of the source code
    type in POT
12) then hit the return 3 additional times
13) when the compiler finishes replace the disk on the left
    with the disk labelled for2
14) type in A:FOR2
15) when this finishes the second pass of the compiler
16) replace the disk on the left with the disk labelled
    FORTRAN LIBRARY
17) type in A:LINK
18) when the linker asks you for the object modules
    type in CRYSTAL+POT
19) hit return 3 times
20) when the linker is finished you should have
    a running program on the disk in the right hand
    drive called CRYSTAL.EXE you can verify this by
    typing in DIR B:
21) copy this onto the disk on the left by typing
    COPY B:CRYSTAL.EXE A:
22) replace the disk on the right with the data disk
type in RUN
If the program doesn't run or gives you garbage there are errors
in the potential function. Also if the compiler returns error
messages you must go back to the editing part of this instruction
and continue from there.

SOURCE CODE FOR POTENTIAL FUNCTION

```
FUNCTION POT(X,Y,Z)
COMMON /PARAM/ ZE,ZO,BD
R2=X*X+Y*Y+Z*Z
R4=R2*R2
T=X*X*X*X+Y*Y*Y*Y+Z*Z*Z*Z-3.0*R4/5.0
POT=35.0*ZE/4.0/(BD**5.0)*T
END
```

RANDOM NUMBER FILE GENERATION

```
10 RANDOMIZE
20 OPEN "RANDOM" FOR OUTPUT AS #1
30 FOR I=1 TO 5003
40 X=RND
50 Y=RND
60 Z=RND
70 PRINT#1,USING".#######";X;Y;Z
80 PRINT USING".#######";X;Y;Z
90 NEXT I
100 BEEP:BEEP:BEEP:BEEP
105 CLOSE#1
110 END
```

```
 cat tink1000
ENTER 04 FOR TETRAHEDRAL COORDINATION
ENTER 06 FOR OCTAHEDRAL  COORDINATION
ENTER 08 FOR 8-FOLD CUBIC COORDINATION
ENTER 12 FOR 12-FOLD CUBIC COORDINATION
ENTER 0 TO RUN WITH INTERNAL PARAMETERS
ENTER 1 TO SPECIFY NEW PARAMETERS
POSITIONING IONS IN THE LATTICE
INITIALIZING CHARGE ON OXYGEN IONS
HOW MANY MONTE-CARLO POINTS (I5) LESS THAN 32000
COMPUTING MATRIX ELEMENT
-0.758011d 00
COMPUTING MATRIX ELEMENT
-0.193706d-01
COMPUTING MATRIX ELEMENT
-0.675547d 00
COMPUTING MATRIX ELEMENT
 0.161519d-01
COMPUTING MATRIX ELEMENT
 0.328048d-01
COMPUTING MATRIX ELEMENT
-0.581051d 00
COMPUTING MATRIX ELEMENT
-0.189928d-01
COMPUTING MATRIX ELEMENT
 0.284910d-01
COMPUTING MATRIX ELEMENT
 0.374327d-02
COMPUTING MATRIX ELEMENT
 0.828496d 00
COMPUTING MATRIX ELEMENT
-0.782377d-01
COMPUTING MATRIX ELEMENT
-0.683282d-01
COMPUTING MATRIX ELEMENT
-0.457849d-01
COMPUTING MATRIX ELEMENT
 0.743769d-01
COMPUTING MATRIX ELEMENT
 0.903533d 00
COMPUTING EIGENVALUES
THE CALCULATION PARAMETERS ARE.....

CHARGE ON OXYGEN  2.00
EFFECTIVE NUCLEAR CHARGE  2.00
LATTICE PARAMETER  2.00
THE EIGENVALUES ARE.....
 0.954882d 00  0.786077d 00 -0.573409d 00 -0.680228d 00 -0.769904d 00
6
1000
2.00
2.00
2.00
 0.954882d 00  0.786077d 00 -0.573409d 00 -0.680228d 00 -0.769904d 00
%
```

37

```
 cat tink4000
ENTER 04 FOR TETRAHEDRAL COORDINATION
ENTER 06 FOR OCTAHEDRAL  COORDINATION
ENTER 08 FOR 8-FOLD CUBIC COORDINATION
ENTER 12 FOR 12-FOLD CUBIC COORDINATION
ENTER 0 TO RUN WITH INTERNAL PARAMETERS
ENTER 1 TO SPECIFY NEW PARAMETERS
POSITIONING IONS IN THE LATTICE
INITIALIZING CHARGE ON OXYGEN IONS
HOW MANY MONTE-CARLO POINTS (I5) LESS THAN 32000
COMPUTING MATRIX ELEMENT
-0.684433d 00
COMPUTING MATRIX ELEMENT
 0.622392d-02
COMPUTING MATRIX ELEMENT
-0.653617d 00
COMPUTING MATRIX ELEMENT
 0.115858d-01
COMPUTING MATRIX ELEMENT
 0.195847d-01
COMPUTING MATRIX ELEMENT
-0.624519d 00
COMPUTING MATRIX ELEMENT
-0.130734d-01
COMPUTING MATRIX ELEMENT
 0.993926d-02
COMPUTING MATRIX ELEMENT
 0.152267d-01
COMPUTING MATRIX ELEMENT
 0.814384d 00
COMPUTING MATRIX ELEMENT
-0.482886d-01
COMPUTING MATRIX ELEMENT
 0.171561d-01
COMPUTING MATRIX ELEMENT
 0.381198d-01
COMPUTING MATRIX ELEMENT
 0.217708d-01
COMPUTING MATRIX ELEMENT
 0.748680d 00
COMPUTING EIGENVALUES
THE CALCULATION PARAMETERS ARE.....

CHARGE ON OXYGEN  2.00
EFFECTIVE NUCLEAR CHARGE  2.00
LATTICE PARAMETER  2.00
THE EIGENVALUES ARE.....
 0.822025d 00  0.744228d 00 -0.613175d 00 -0.663467d 00 -0.689116d 00
 6
 4000
2.00
2.00
2.00
 0.822025d 00  0.744228d 00 -0.613175d 00 -0.663467d 00 -0.689116d 00
%
```

```
 cat tink32000
ENTER 04 FOR TETRAHEDRAL COORDINATION
ENTER 06 FOR OCTAHEDRAL  COORDINATION
ENTER 08 FOR 8-FOLD CUBIC COORDINATION
ENTER 12 FOR 12-FOLD CUBIC COORDINATION
ENTER 0 TO RUN WITH INTERNAL PARAMETERS
ENTER 1 TO SPECIFY NEW PARAMETERS
POSITIONING IONS IN THE LATTICE
INITIALIZING CHARGE ON OXYGEN IONS
HOW MANY MONTE-CARLO POINTS (I5) LESS THAN 32000
COMPUTING MATRIX ELEMENT
-0.614619d 00
COMPUTING MATRIX ELEMENT
-0.197246d-02
COMPUTING MATRIX ELEMENT
-0.627631d 00
COMPUTING MATRIX ELEMENT
-0.187123d-01
COMPUTING MATRIX ELEMENT
-0.181665d-01
COMPUTING MATRIX ELEMENT
-0.611702d 00
COMPUTING MATRIX ELEMENT
-0.124754d-02
COMPUTING MATRIX ELEMENT
 0.927798d-02
COMPUTING MATRIX ELEMENT
-0.952971d-02
COMPUTING MATRIX ELEMENT
 0.801265d 00
COMPUTING MATRIX ELEMENT
 0.578322d-03
COMPUTING MATRIX ELEMENT
 0.122425d-01
COMPUTING MATRIX ELEMENT
-0.224950d-02
COMPUTING MATRIX ELEMENT
-0.619347d-02
COMPUTING MATRIX ELEMENT
 0.788407d 00
COMPUTING EIGENVALUES
THE CALCULATION PARAMETERS ARE.....

CHARGE ON OXYGEN  2.00
EFFECTIVE NUCLEAR CHARGE  2.00
LATTICE PARAMETER  2.00
THE EIGENVALUES ARE.....
 0.803822d 00  0.786089d 00 -0.590134d 00 -0.619015d 00 -0.645042d 00
6
32000
2.00
2.00
2.00
 0.803822d 00  0.786089d 00 -0.590134d 00 -0.619015d 00 -0.645042d 00
%
```

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