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MICROGRAVITY SCIENCE AT LANGLEY RESEARCH CENTER

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INTRODUCTION

The Microgravity Science effort at the Langley Research Center is centered on the growth of the compound semiconductor alloy, lead tin telluride. Lead tin telluride is a substitutional alloy of lead telluride and tin telluride that is miscible over the entire compositional range. The semiconductor properties of this material are dependent on the ratio of the two components and consequently, the uniformity of an array of devices is dependent on good compositional control[1].

This material was chosen for microgravity research because of a number of reasons. Lead tin telluride is not only a useful semiconductor material which has been used for construction of infrared detectors and tunable diode lasers but it also has a similar phase diagram to other compound semiconductors of interest such as mercury cadmium telluride and mercury zinc telluride. Lead tin telluride is very interesting from a purely scientific point of view in that it is both solutially and thermally unstable but,in a one dimensional analysis with growth axis parallel to the gravity vector, only one instability works, per orientation, at a time. This double convective instability can not be made stable by balancing thermal and solutal expansion in a high temperature gradient[2]. Lead tin telluride is amenable to study for it is easily compounded, it has a relatively low vapor pressure, it is single phase and there is existing, though limited, literature on its growth and properties.

The Langley effort consists of both ground based and flight research. This paper will concentrate on the flight effort with

reference to the ground based effort only when necessary for clarity.

MATERIALS PROPERTIES

The composition of lead tin telluride chosen for flight experiments is 20% SnTe and 80% PbTe. At this composition the segregation coefficient is 0.7 and the material will begin to solidify at 904°C. The steady state temperature, if steady state could be reached, is 894°C.

The properties of lead tin telluride that make it interesting for space processing are its coefficients of thermal and solutal expansion of the liquid phase. These coefficients are of course functions of both temperature and composition but values at the melting point of $Pb_{.8}Sn_{.2}Te$ are 118×10^{-6}/°C and -0.23/mole fraction SnTe. These are relatively large values and hence will produce a large driving force for convection in a gravity field. Note that the expansion is in opposite directions at the melt-solid interface such that even in a one dimensional analysis there can be no stable orientation.

A more complete listing of materials properties can be found in reference 3.

SCIENCE REQUIREMENTS

The solute distribution in a directionally solidified crystal is quantitatively given by equations of Smith et al[4] and Tiller et al[5] if the only mixing in the liquid is through diffusion. If the liquid is mixed with fluid velocities that greatly exceed the interface velocity, e.s. strong convection. then the solute distribution is given by the normal freeze equation[6]. Solidification configurations in which both diffusion and other mixing forces are needed to describe the model are amenable to analytical solutions only in a few special cases[7]. Figure 1. shows the calculated solute distribution for 20% SnTe for the two extreme cases. This figure shows that between an initial and a final transient the crystal composition is constant if the fluid motion is governed only by diffusion where as there are no regions of constant composition in the growth where the liquid is totally mixed. Figure 2. shows the compositional profile of an Earth based growth. This result, which matches growth from a highly mixed liquid, is always obtained for ground based growth.

The desired growth mode is of course one in which convection is zero so compositional steady state can be reached. However fluid dynamic calculations[8] have shown that finite convection exists in the physical configuration used in crystal growth experiments even at 1×10^{-8} Earth gravity if there is a density gradient orthogonal to the gravity vector. It has also been calculated[7] that due to the residual atmosphere the minimum gravity level expected on the Space Shuttle is on the order of

$1x10^{-5}$ Earth gravity even at the center of mass of the craft. From this brief discussion, fluid motion can be expected in the Microgravity experiments and the experimental objectives become ways of determining how much convection exists under what driving forces and what is the effect of the convection.

An ideal microgravity crystal growth experiment would require control of the interface shape and position[10,11] growth rate (not just ampoule translation rate), axial and radial temperature gradients and the residual body force vector. The desired analysis procedures would include not only the normal post growth procedures but also in situ measurements of fluid velocities and interface position and shape. Not all of these controls and measurements will not be available for either MEA or AADSF experiments but progress is being made to at least incorporate the measurements in the Earth based growth of lead tin telluride at Langley. The interface movement with respect to ampoule position in the furnace and axial temperature gradients have been measured as a function of furnace profiles[12]. X and gamma rays have been used to measure thermocouple movement in the furnace as well as the interface position and shape[13]. An electrochemical technique of titrating trace amounts of oxygen through a solid electrolyte into the ampoule and then measuring its time of travel between electrodes is being used to measure the fluid motion[14].

FLIGHT EXPERIMENTS

A flight opportunity has been made available in the MEA furnace and additional flight opportunities are anticipated in both the MEA and the AADSF. Each of these experiments will be described separately below.

MEA

The Materials Experiment Assembly (MEA) is a stationary, i.e. no ampoule translation, furnace with either one (isothermal model) or three (gradient model) temperature zones and a water cooled block at one end. A helium quench is available if desired. Each zone in the gradient model can be independently controlled and the maximum temperature is approximately 1000°C.

Furnace characterization is important for any crystal growth experiment but it is especially vital for a stationary furnace such as MEA in which a temperature gradient is to be translated through the furnace at a constant rate. To this end an instrumented inert (SiO_2) cartridge with thermal properties similar to lead tin telluride was constructed and ground based tests were conducted in the flight furnace. The maximum temperature gradient, at the solidus temperature, that could be maintained over the length of the cartridge was 20°C/cm hence the growth rate needed to be keep below 3.5mm/hr to prevent interfacial breakdown[15]. The growth rate was derived by carefully profiling the furnace at various zone settings and then

determining both the zone temperatures and the time between these settings which would translate a 900°C isotherm through the cartridge at a constant 3.5mm/hr after the cooling water was turned on to initiate growth. Figure 3. shows the chosen furnace temperature profile for the three zones and Figure 4. shows the translation of the desired isotherm through the SiO_2 sample in ground based tests.

The flight sample was a quenched polycrystalline boule that was compounded from the elements. A quenched sample was chosen because even though such sample exhibits large microsegregation the macrosegregation is lower than a ground based directionally solidified sample hence diffusion alone could homogenize the melted sample. The ampoule was 2mm thick fused silica with a 6mm fused silica plug sealed in each end. The MEA instrumentation allowed for two monitoring thermocouples which were placed in groves on the ampoule. The ampoule was then placed in a stainless steel sheath for insertion into the furnace.

The experiment was performed on Shuttle Flight STS 61A in October 1985. The MEA furnace was returned to MSFC and it was opened to retrieve and return samples to the investigators on December 4,1985. The ampoule was removed from the metal sheath at MSFC and then taken back to Langley for analysis.

The primary concerns in analysis are the axial composition distribution and the observation of voids, if any, in the crystal. The axial composition will indicate the extent of deviation from planar, diffusion controlled, growth. Voids have occurred in Earth grown samples when the growth direction was parallel with the gravity vector.

The crystal was examined for voids using gamma radiation before the ampoule was opened. No voids were observed. The ampoule was opened by cutting the quartz with a wire saw.

In order to examine the axial composition the crystal had to be cut along its axis and polished. The first and ,to date, only cut position was chosen to not only bisect the crystal through the center axis of the ampoule but also to bisect a small mound on the free surface of the crystal.

The composition of the crystal was measured with a wavelength dispersive electron microprobe. Axial data is shown in figure 5. The continuous curve is the calculated values of SnTe concentration if the liquid was continuously and totally mixed during solidification. As can be seen, the data is a reasonable match to the mixed curve in the region between 2mm and approximately 38mm. The first 2mm follows the anticipated thermal supercooling curve that is explained in a previous paper[16]. The extent of apparent mixing shown in the next 34mm was not expected. Although apparent mixing can result from a number of factors such as a non-planar interface, time variations in growth rate, a very slow growth rate where the diffusion barrier extends the length of the ampoule and ,of course, convective driving

forces it is probable that the main contributor was convection even though the gravity level was on the order of 1×10^{-4} Earth gravity.

Post flight analysis of the furnace, performed by MSFC engineers, determined that the cooling water loop did not function as planned. This is a primary concern became the programed time evolution of the sample temperature, hence growth rate, was determined with the cooling water operational. Knowledge of the growth rate is vital to the thorough analysis of the experiment.

The furnace was to start its electrical cool down shortly before the start of the coolant flow. The advent of the coolant would produce a 40°C drop in temperature at the base of the melt to start the solidification process. The furnace was programed to provide a steady growth rate from that time. The lack of a coolant, of course, changes the growth rate. Additional calibration runs are being conducted to determine the actual growth rates that occurred under flight conditions. However, a certain amount of speculation can be made based on the available data.

One possible explanation for shape of the composition vs distance at 38mm is as follows. Due to lack of cooling water crystal growth begin three hours later (see the 904°C isotherm in figure 6) than expected but the furnace still went into a power down mode as programed. Figure 6 shows that the number two thermocouple (T2 in Fig.6) was reading approximately 35°C above the melt point when the center furnace (TM in Fig.6) turned off. Hence there was a rapid increase in growth rate when the interface was in the vicinity of T2. Figure 7. shows an initial and a final transient curve for diffusion controlled growth with a growth rate of 35mm/hr superimposed on the data. The hypothesis is that the increased growth rate due to the furnace shut down was sufficient to overcome the fluid velocity due to convection and a transition from convection controlled growth to diffusion controlled growth occurred. The variation in composition after this point may be due to interface breakdown which would be expected to occur in diffusion controlled growth and the G/R ratio of the higher growth rate.

The observation of a transition from convection controlled growth to diffusion controlled growth would be very significant to microgravity science if it can be verified. The first step toward verification is the calibrate the MEA furnace for the actual flight conditions and the second step is to perform the growth in space with different growth rates.

AADSF

The advanced automated directional solidification furnace (AADSF) represents a significant improvement over the MEA. The most obvious improvement is an ampoule translation mechanism; the

lack of which has produced the greatest uncertainty in the MEA experiment. The second most important improvement is an insulated zone between the hot and cold zones which along with a higher temperature capability (>1150°C) will produce axial temperature gradients of 100°C/cm or greater.

The precise tests that will run in the AADSF will be influenced by the evolving analysis of the MEA sample and the results of the continued ground based work. However the best idea at present is to conduct a series of crystal growth experiments in which the growth rate is varied between runs. The slowest growth rate of interest would be that designed for the MEA flight, 3.5mm/hr. Higher growth rates would be matched to calculated fluid velocities[8] but limited by the need to preserve interface stability as calculated for the furnace temperature gradient. The lead tin telluride fluid velocity will decrease with decreasing body force levels but it is expected to be finite on the Space Shuttle regardless of operational mode. Hence the attainment of compositional steady state will controlled by both the configuration of convection cells (a low velocity cell near the interface will form a barrier to a high velocity, counter rotating cell that is higher in the ampoule) and the relative velocity of the fluid and the interface.

CONTINUED GROUND BASED RESEARCH

Even though flight opportunities are absolutely necessary for continued development of Microgravity Science there is also a strong need for continued ground based research. Crystal growth has to be continuously developed from an art and turned more into a science. The Microgravity Science program has been a leader in this effort especially in getting crystal growers to think in terms of fluid mechanics.

The field of fluid mechanics applied to crystal growth has a great potential for near term payoff. Progress is being made through this laboratory and elsewhere[8,11,17] but the solutions of the fluid dynamic equations as applied to physical growth systems are still in an embryonic state. More and continued research is needed not only in the calculations but also in confirming measurements of both heat and fluid flow.

Another area that needs additional attention is the effect of interface shape on crystal growth. The interface shape of a crystal being grown by directional solidification is controlled by a combination of heat flow patterns and the thermophysical properties of the material and the extent of convection in the liquid. The interface shape, in turn, can have a pronounced effect on the diffusion and convection patterns of the rejected solute as well as defect density and dopant concentration in the final crystal. That is, interface shape and dopant/solute convection are interactive in that one affects the other.

Interface demarcation with Peltier pulsing has shown a two dimensional image of the three dimensional interface[18,19]. This technique has produced a wealth of scientific data but it is limited to a select few semiconductor crystals. Chemical etching after growth will show the extent of turbulence and meltback on some crystals when such conditions occur[20].

A technique using X and gamma radiation to observe the interface during growth has been developed at Langley[13]. This technique has been successfully demonstrated on both germanium and lead-tin-telluride to observe and control the interface position but additional effort is needed to go beyond semi-quantification of the interface shape.

SUMMARY

Although space research is still in an embryonic state a combination of Earth based and space flight experiments are being coupled to yield a better understanding of the complex interaction of heat and fluid flow on the dynamics of crystal growth. Continued efforts on the ground as well as additional flight opportunities are needed to continue the drive to fully understand the advantages, both scientifically and economically, of microgravity crystal growth.

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FIGURE CAPTIONS

Figure 1. Calculated curves of solute distribution in directional solidified $Pb_{.8}Sn_{.2}Te$ for both diffusion and convection controlled growth. The length and growth rate are chosen to be compatable to the MEA experiment.

Figure 2. Microprobe data of composition vs distance for a typical Earth grown crystal of $Pb_{.8}Sn_{.2}Te$. The solid curve is from the normal freeze equation.

Figure 3. Temperature control settings for the three zone MEA furnace. TH refers to the zone furtherest away from the cooling block. TM refers to the center zone and TC is for the zone adjacent to the cooling block.

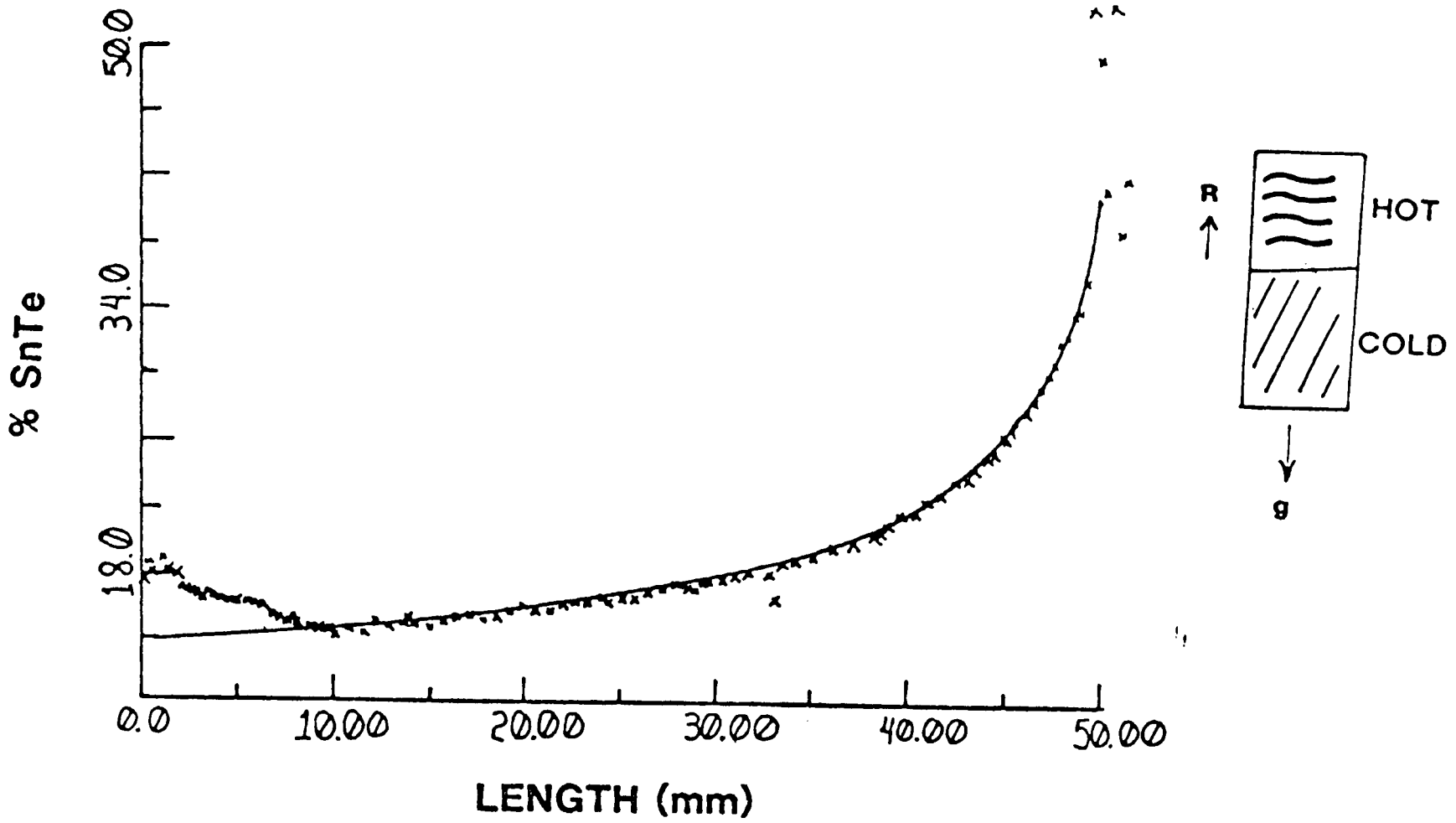
Figure 4. Position of the 900°C isotherm as a function of time. Measurement was made on the ground but in the flight furnace. The sample was an instrumented SiO_2 cylinder the size of the flight cartridge.

Figure 5. Microprobe data of composition vs distance. Each scan is parallel to the ampoule center line but are separated by 3.7mm. The solid curve is calculated from the normal freeze equation.

Figure 6. Temperature data for the MAE A2 flight. Curves marked TH, TM and TC are furnace thermocouple data from the zones as described in Figure 3. The data marked T1 and T2 are from thermocouples attached to the ampoule.

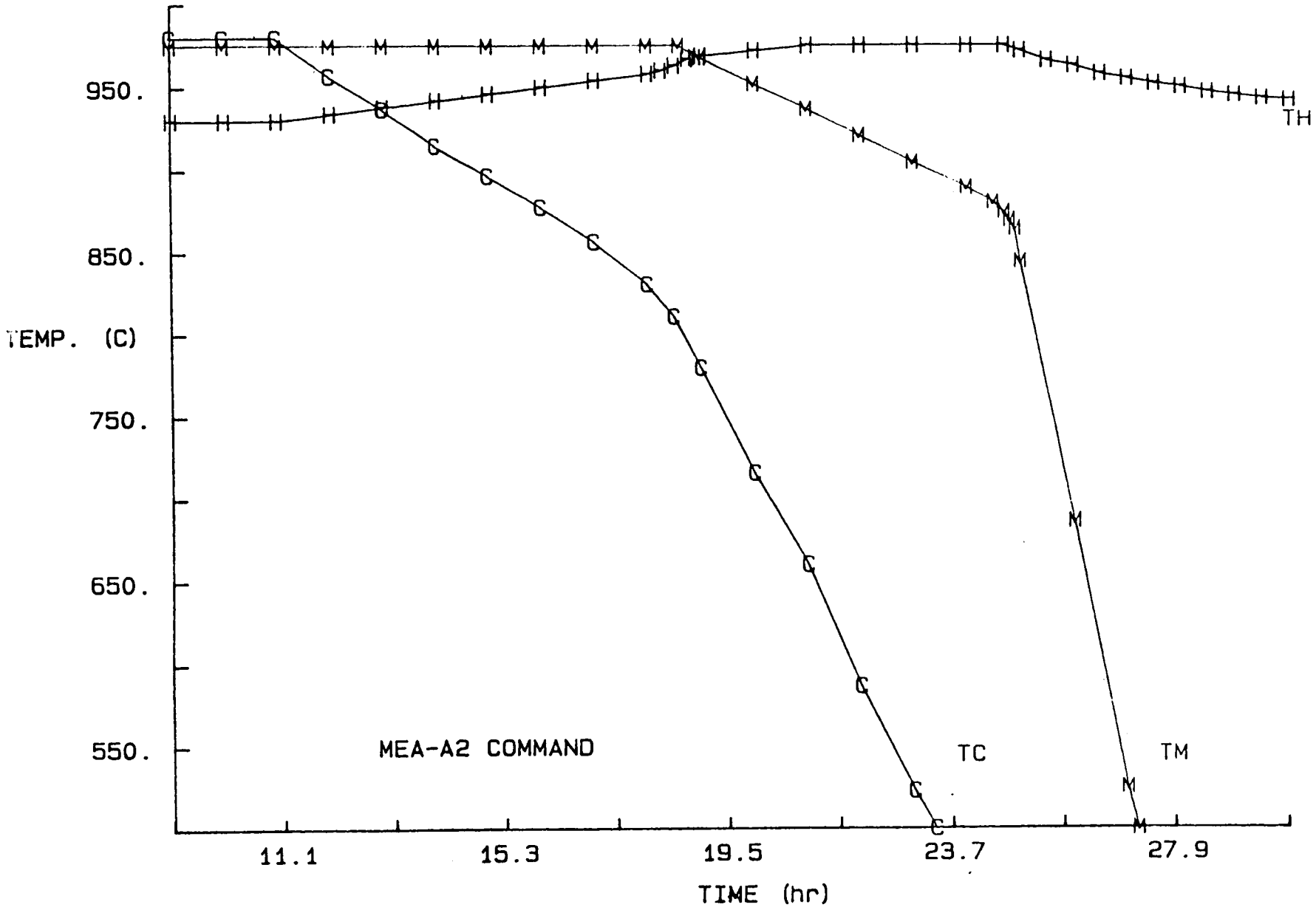
Figure 7. The data is the same as figure 5. The solid curves are the initial and final transients if the growth changed from convection controled to diffusion controlled growth.

DIFFUSION CONTROLLED
MIXED
LENGTH (cm)
0.0
1.2
2.4
3.6
4.8
6.0
10.0
14.0
18.0
22.0
26.0
30.0
Xsn/a

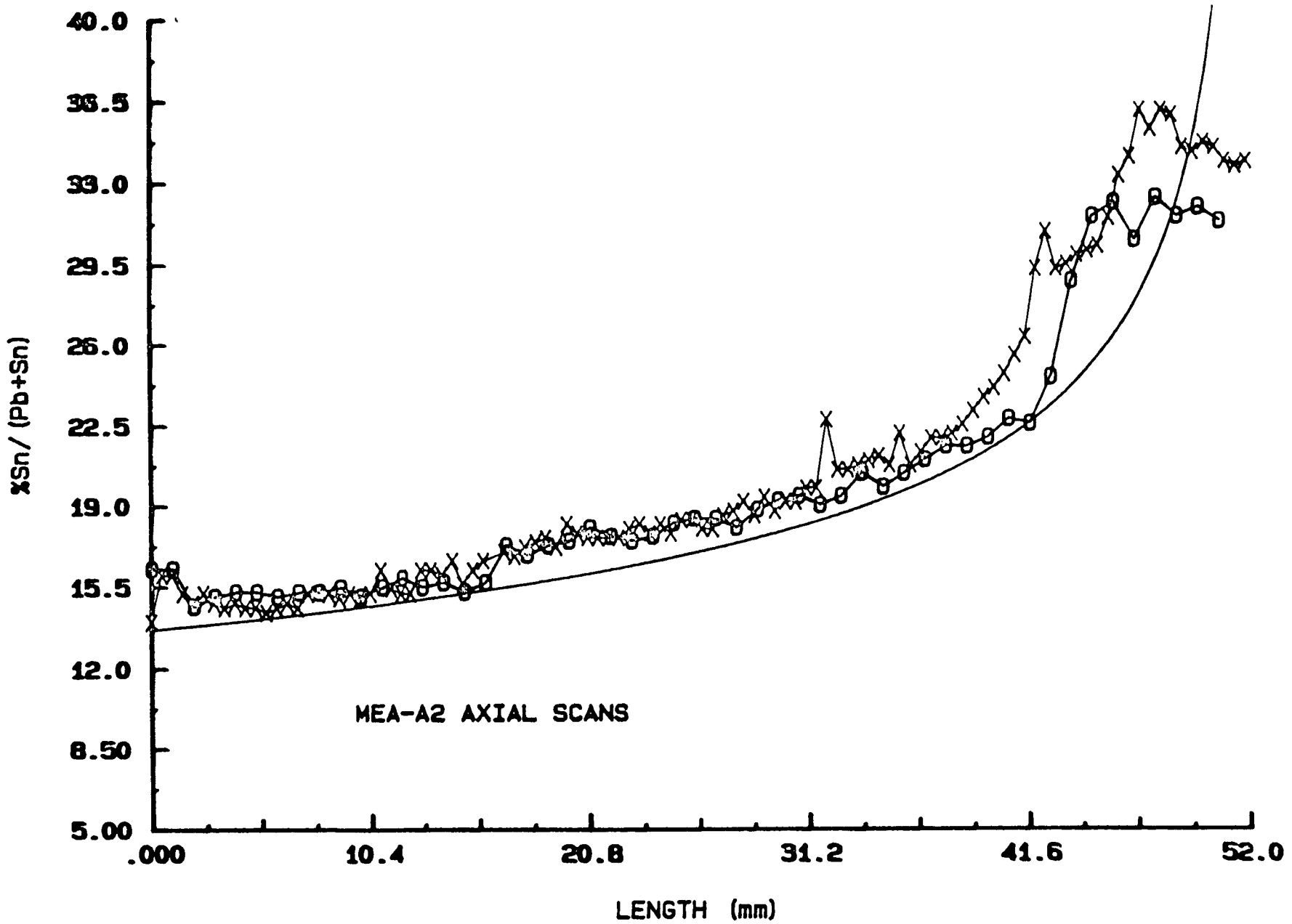

50.0
34.0
18.0
% SnTe
0.0
10.00
20.00
30.00
40.00
50.00
LENGTH (mm)
R
HOT
COLD
g

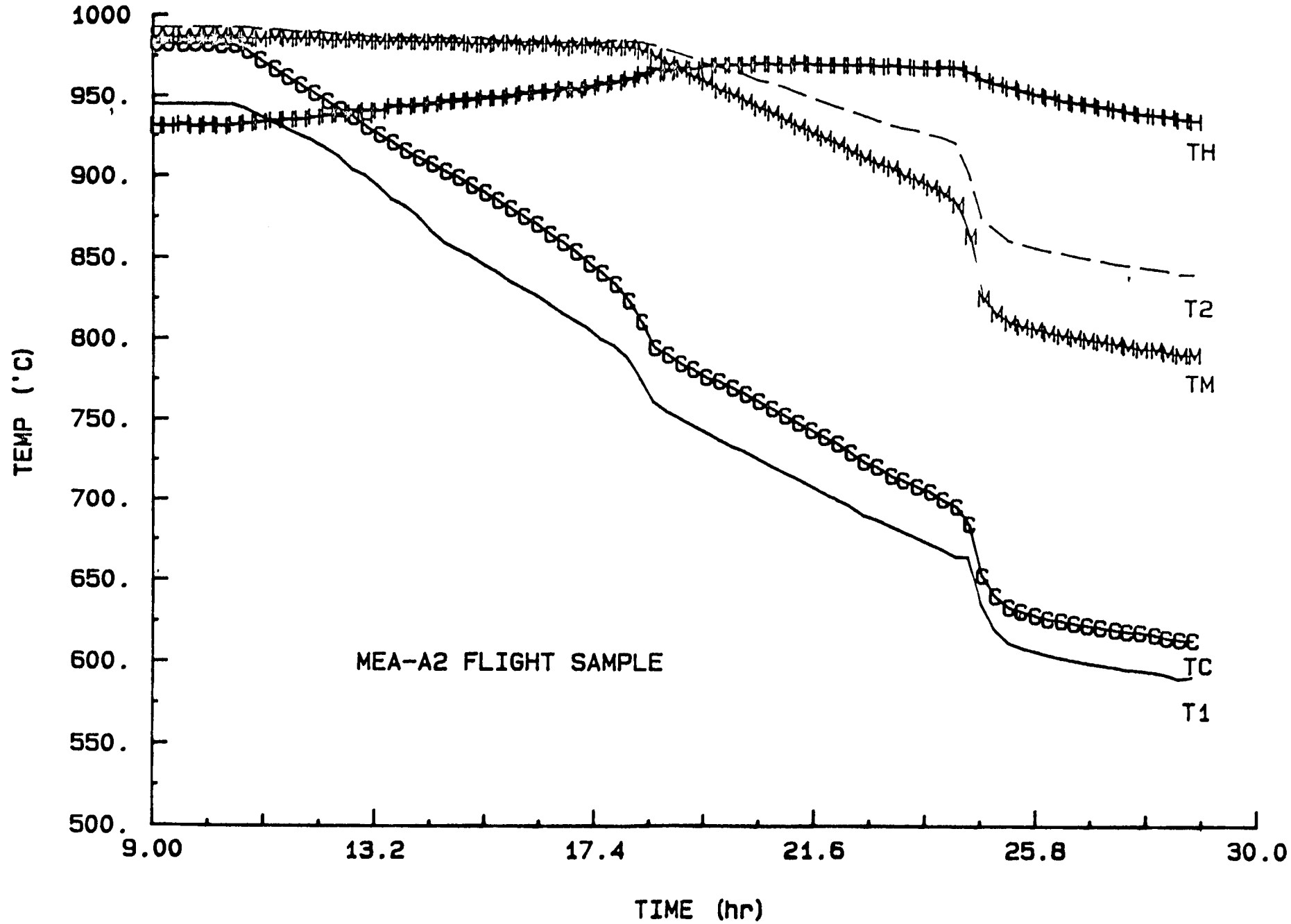
402

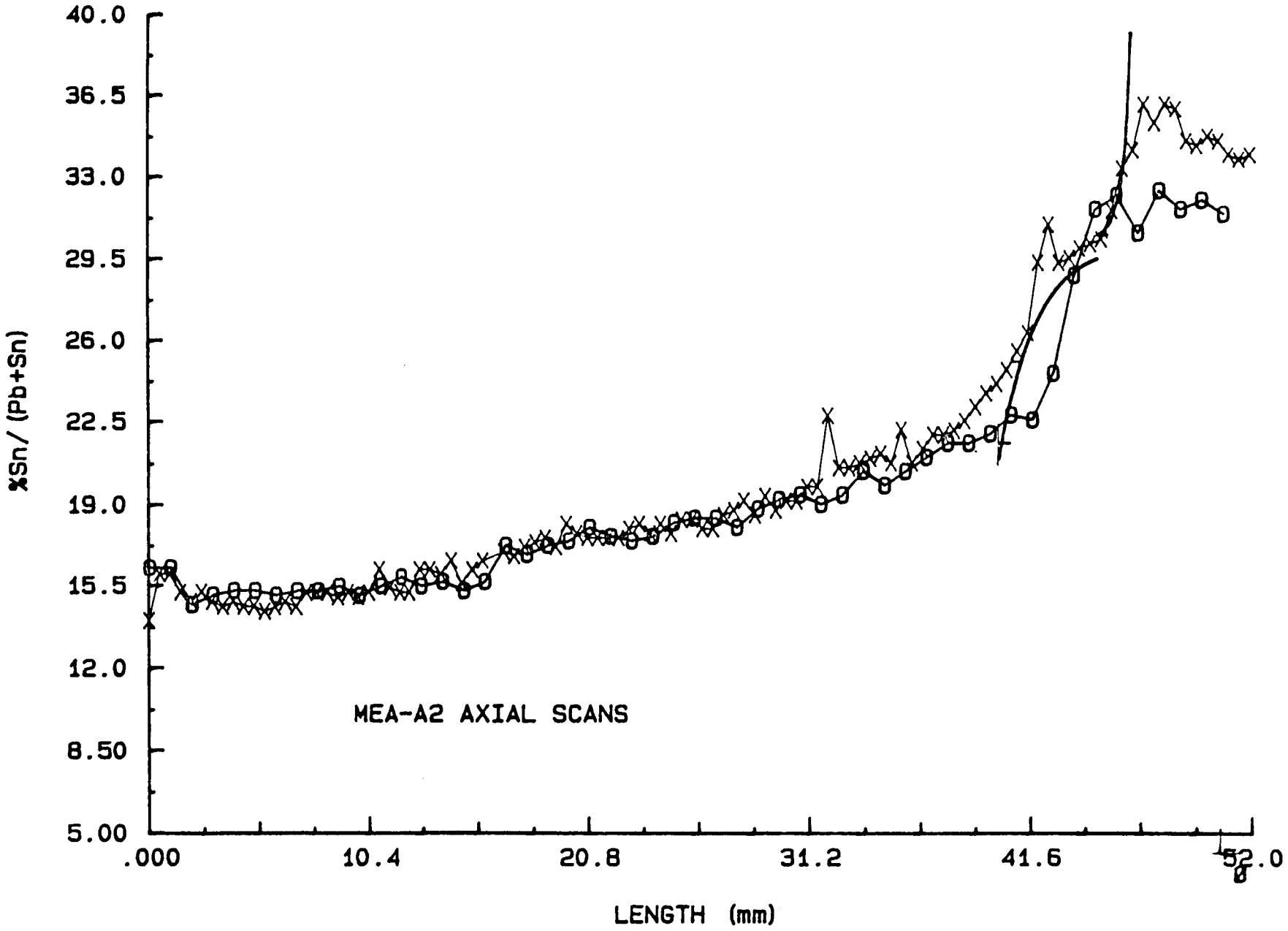
Fig 2


950.
850.
750.
650.
550.
TEMP. (C)
MEA-A2 COMMAND
TC
TM
TH
11.1
15.3
19.5
23.7
27.9
TIME (hr)

POSITION (cm)
2.0
4.0
6.0
8.0
10.0
TIME (hr)
10.00
14.00
18.00
22.00
26.00
30.00


40.0
36.5
33.0
29.5
26.0
22.5
19.0
15.5
12.0
8.50
5.00
%Sn/ (Pb+Sn)
.000
10.4
20.8
31.2
41.6
52.0
LENGTH (mm)
MEA-A2 AXIAL SCANS


1000
950.
900.
850.
800.
750.
700.
650.
600.
550.
500.
TEMP ('C)
9.00
13.2
17.4
21.6
25.8
30.0
TIME (hr)
TH
T2
TM
TC
T1
MEA-A2 FLIGHT SAMPLE


40.0
36.5
33.0
29.5
26.0
22.5
19.0
15.5
12.0
8.50
5.00
%Sn/ (Pb+Sn)
MEA-A2 AXIAL SCANS
.000
10.4
20.8
31.2
41.6
52.0
LENGTH (mm)