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# Cellular Solidification of Transparent Monotectics

A Semi-annual Report for NAG8-069

by

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## INTRODUCTION

Understanding how liquid phase particles are engulfed or pushed during freezing of a monotectic is the problem addressed by this research. The additional complication is that the solid-liquid interface is non-planar due to constitutional undercooling. Some evidence of particle pushing where the particles are the liquid<sub>2</sub> phase of the monotectic was already observed. Cellular freezing of the succinonitrile-glycerol system also occurred. Only a few compositions were tested at that time. The starting materials were not especially pure so the cellular interface observed was likely due to the presence of unknown impurities the major portion of which was water.

The work described here will cover:

- a) the effort of modeling the particle pushing process using the computer,
- b) establishing an apparatus for the determination of phase diagrams,
- c) the measurement of the temperature gradients a with which a

specimen will solidify on the temperature gradient microscope stage.

#### PARTICLE PUSHING MODEL EFFORT

Encouraging results were obtained from the models developed using the TK! Solver software purchased for this project. Three versions of the model were prepared. One model based on a paper by Bolling & Cisse (JCG 10, 1971) was used, where particles were pushed by a solidification front under the different conditions of particle size and roughness, melt viscosity, interface velocity, and gravity. Another paper describes another similar derivation of the relationship between particles and the interface but without gravity. This paper was by Chernov et al (Sov. Phy. Crys. 21,1976). For both of these analyses, the particle is solid and relatively inert with respect to the melt. In another paper by Derby presented at ESA Materials Science Symposium, 1983, the Chernov analysis is employed. The particle is now the second phase liquid of the monotectic and the particle-interface interaction handled by balancing the interfacial energies. Some values for the interfacial energies of metal monotectics are also given and used to test their model.

All three models bear striking similarity to one another. The critical formulae for each was introduced to the TK! Solver format and various solutions were tested. The desired combination of interfacial energy balance and the inclusion of gravity effects was not available from these models. A fourth model was assembled from the salient parts of the other three and used a first-principles ap-

proach. This is the Kaukler & Curreni model. In this latter model, each of the forces which compete during particle pushing was found separately rather than simultaneously. A simple force balance did not however yield a reasonable critical velocity for pushing of a particle of a certain size. This was also the case for the other models when numbers other than those used by the authors were introduced to their model. It is too early to tell if the model formulae for any of these are correct or inherently misused. The relationships obtained from solving the models are qualitatively correct.

The Bolling & Cisse model was the first tested. In addition to their basic particle pushing formulae, values for melt composition, temperature, viscosity, density and interfacial energy were added. The enhanced model allows entry of composition and temperature for the system Al-In-Sn and yields a critical velocity for a given particle size. By weaving the models together, these parameters can be exchanged and introduced to other models. Included with this report is a plot of the relationship between critical velocity, viscosity of melt and of temperature for a 10 micron particle using the enhanced Bolling & Cisse model. Their model that includes gravity was not able to reproduce the results from their own data. The model used for this plot does work with their own data. The plot information is that for the Al-In-Sn data used. The problem is that the critical velocity is too great for the conditions expected.

More work on refining these models and of enhancing them to allow comparison is still going on. Then, once a planar interface is modeled, the complication of having a cellular interface can be

added. This problem can already be handled by looking at Bolling & Cisse again. They observed that particles were more likely to be pushed at grain boundaries or cusps since two or more points of contact could be established rather than one (as in the planar case). They offer a quantitative estimate for the increase of the critical velocity attained under these circumstances. We then will have a model of the phenomenon we are trying to observe experimentally.

#### PHASE DIAGRAM DETERMINATION

An apparatus was assembled to perform precise determination of the phase transition temperatures for these organic solutions that are being grown in this study. The device consists of a jacketed specimen vessel which has a stir-bar and a precision platinum resistance thermometer element. The temperature reads accurately to 2 milli-degrees and the digital output will be read into the computer directly via IEEE bus. The IEEE input card has been ordered. The bath will circulate coolant through the jacket and a microprocessor will program the temperature ramp of the bath. The transition temperatures will then be determined during the slow cooling from an elevated temperature. A schematic diagram of this system is given at the end.

This apparatus is needed to determine the phase diagram data needed for this work. More significantly, the changes to the diagram when a ternary addition is made need to be quantified. Then, the cellular transition and the volume of particles can be

calculated.

#### TEMPERATURE GRADIENT MEASUREMENTS

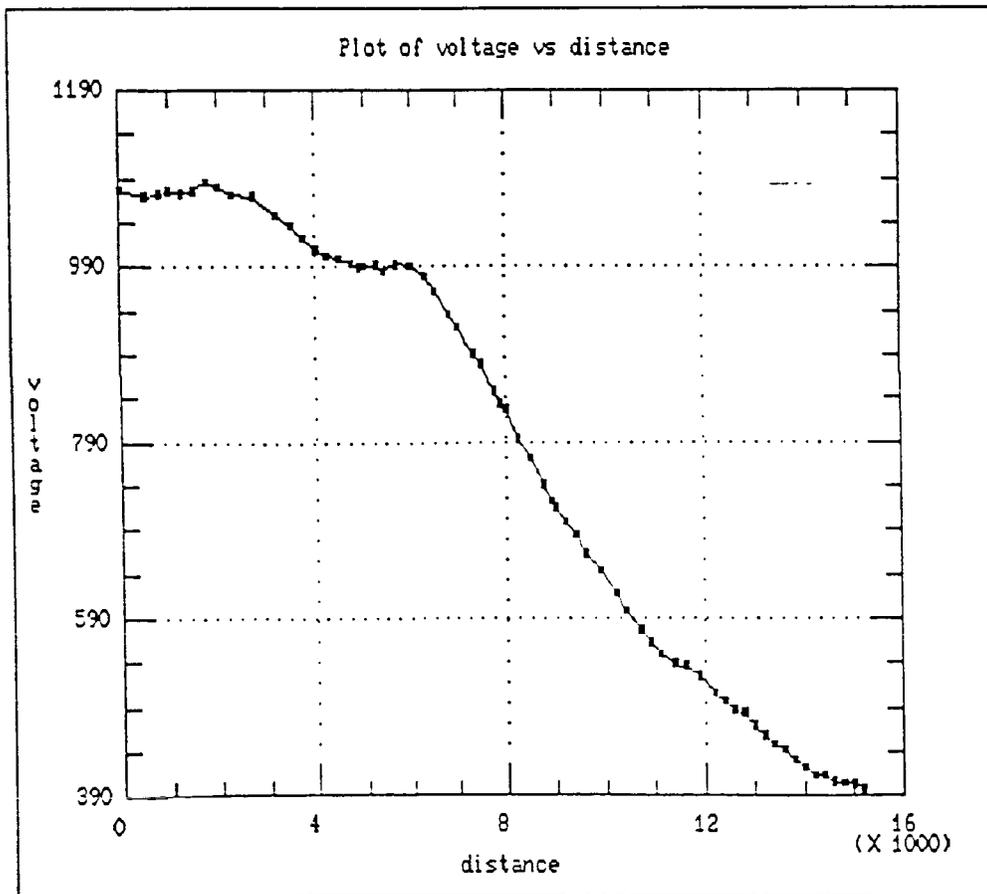
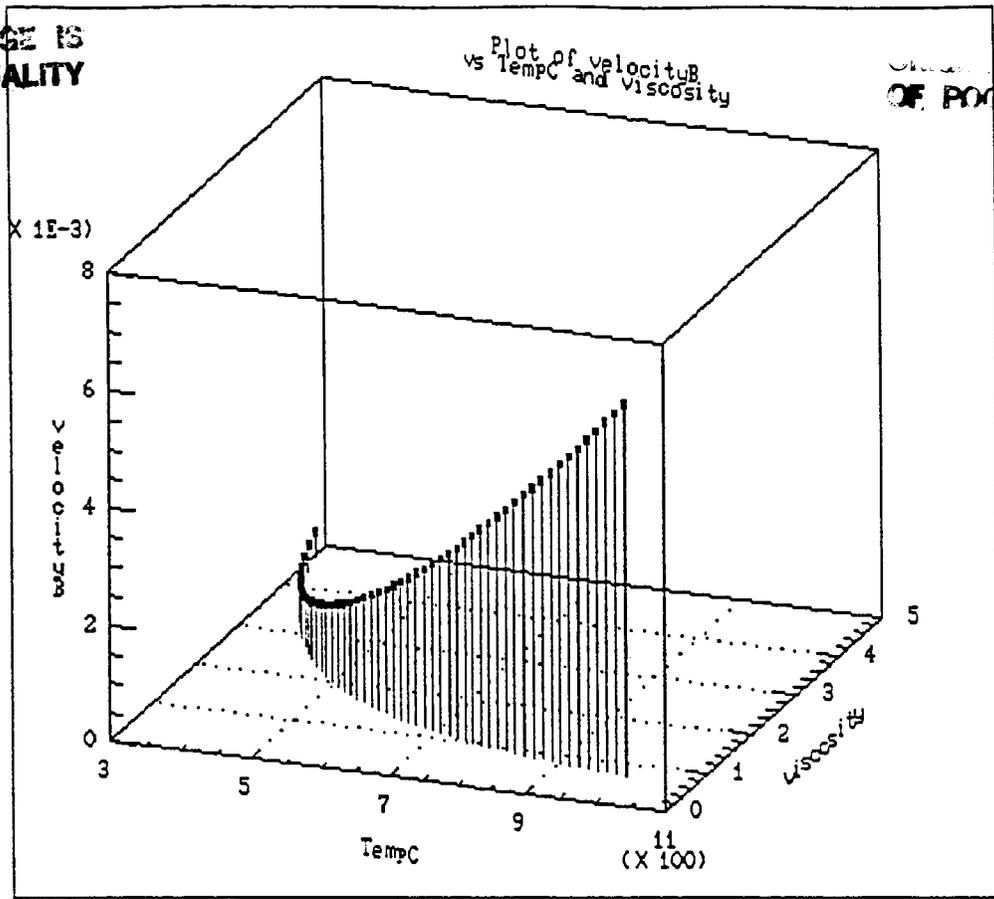
A simulation cell with an incorporated thermocouple was constructed to perform the measurements of the temperature gradient observed by the sample during growth. We can measure the individual block temperatures of the hot-cold surfaces that create the temperature gradient and across which the sample sits. The conduction of heat through the sample cell establishes the gradient. The thickness of the cell walls determines the rate of heat flow. The best way to determine the gradient was to measure it rather than to model it. For this, a cell was constructed from the same glass slides as any specimen would be. Epoxy was used for the specimen contents and also to fix the miniature thermocouple in place. The cell was driven along the stage surface as if it were a specimen being grown. During its transition, readings of its position and of the voltage on the thermocouple were taken (by hand). The rate of translation also affects the temperature at the thermocouple since heat may diffuse more slowly than the cell be translated. Since these effects would be difficult and time consuming to model, these effects were measured directly. The temperature readings were taken at different push rates. One push rate was a stop-start type where a small translation of about 100 micrometers was followed by a stop of a minute or two until the temperature stabilized. Then the process was repeated for a total translation of 18 mm. This establishes the

equilibrium gradient. The data was entered in the computer and reduced to give the temperature gradient. The theoretical gradient (no sample cell) was set to both 100 and 75 deg. /cm. The translation rates were 0, 5.0844, 16.368, and 168.13 micrometers/sec. The measured gradients were found always to be less than 22 deg./cm and more than 15 deg. /cm. A table of the data is included at the end.

#### SUMMARY

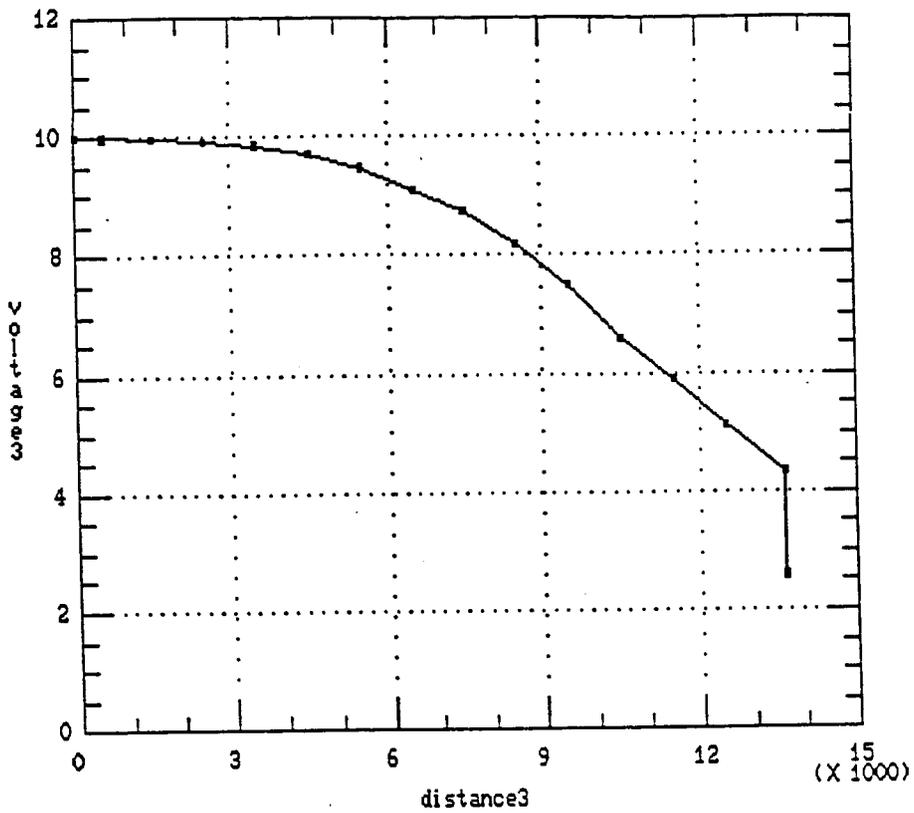
Work has progressed on the particle pushing models, measurements of the temperature gradients for different growth rates, and setting up of a specialized apparatus to determine phase diagram data. This is on-going work and will continue. The models are not yet at a stage where they would be useful to apply to our systems. The gradient data is a crucial part of the growth experiments. The phase diagram data will be taken periodically as time goes on because the solutions change character with time. A fresh solution needs to be made prior to growth testing and then a datum for the diagram can be taken.

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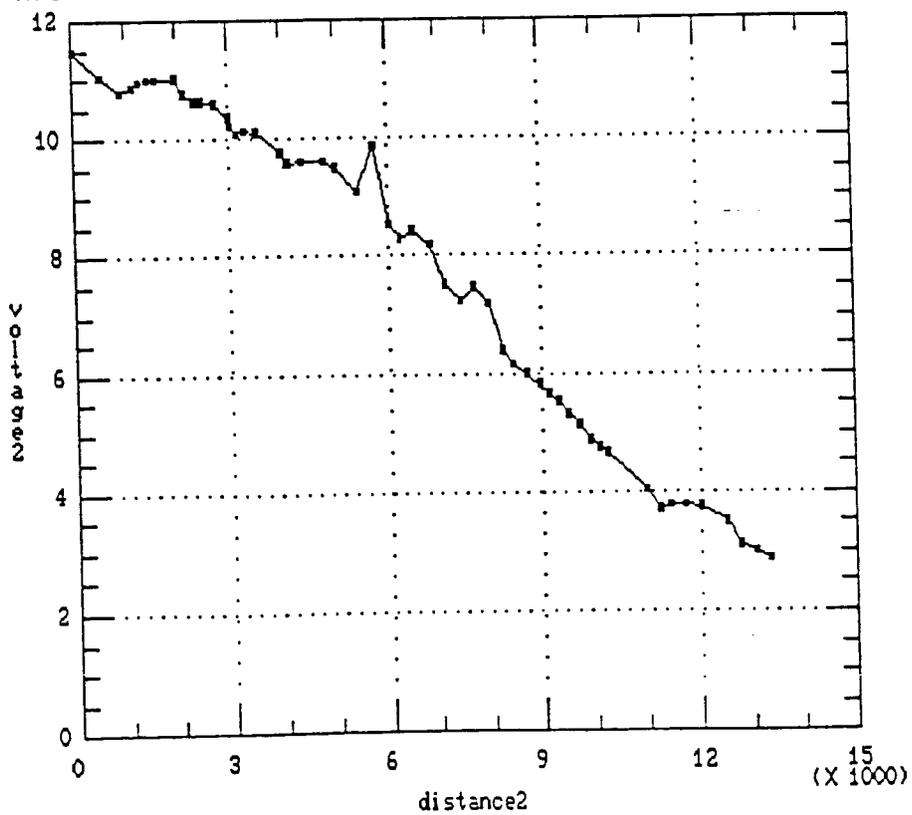
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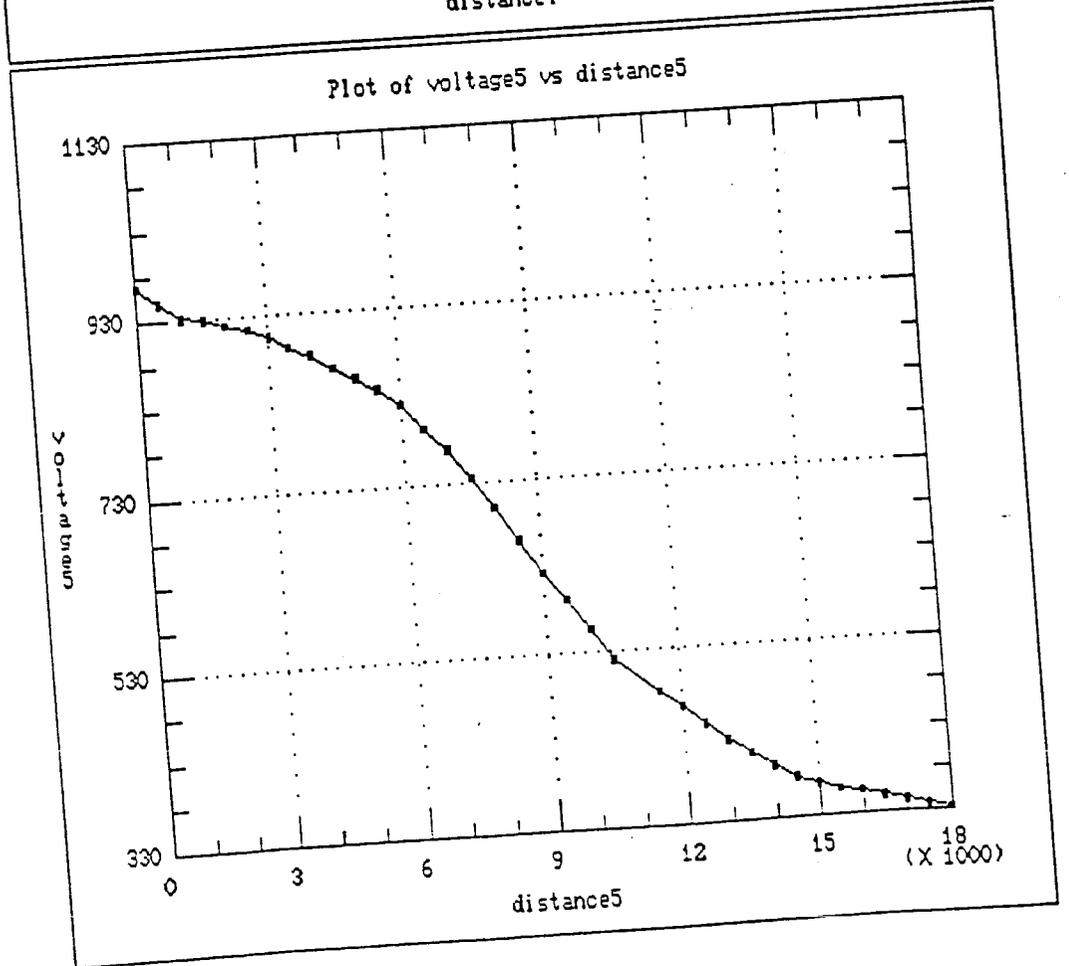
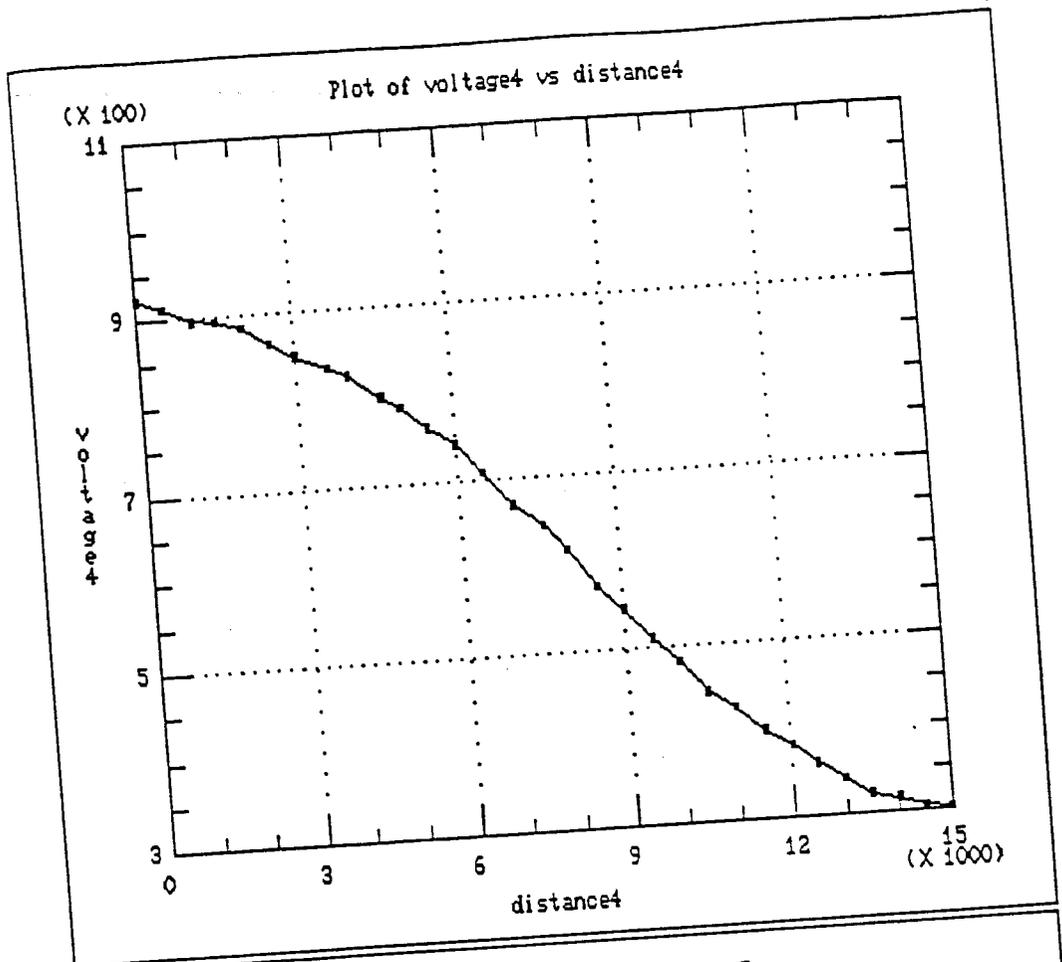
Plot of voltage3 vs distance3



(X 100)

Plot of voltage2 vs distance2

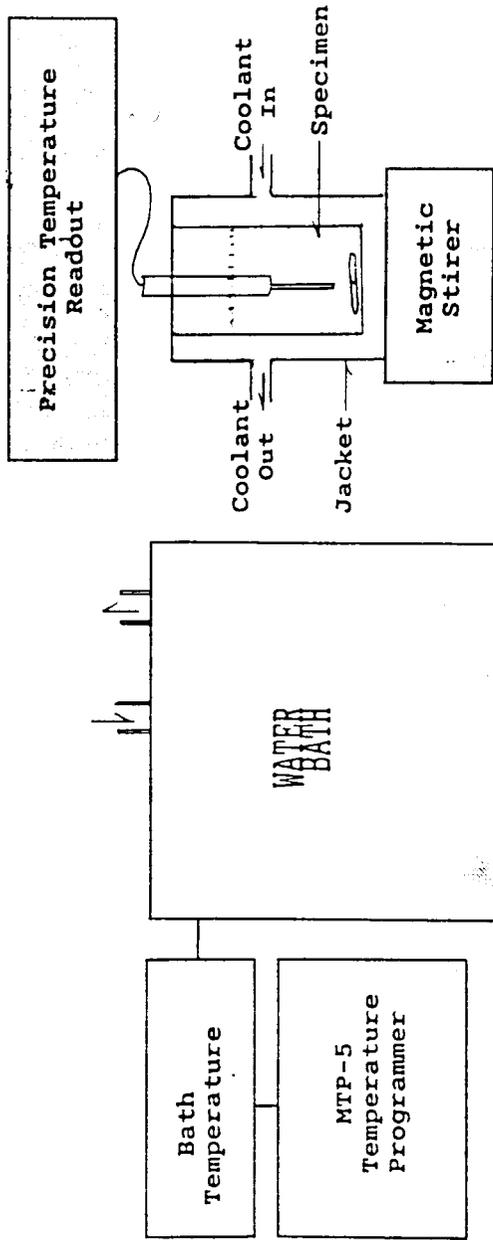




Gradient Measurements on VTGS

slope	stand err	calc grad	std err	spline na
-0.08925	0.0015	-21.0698	0.354105	d/vspline
-0.08106	0.00266	-19.1365	0.6279462	d2v2splin
		0	0	d3v3splin
-0.06398	0.00107	-15.1051	0.2525949	d4v4splin
-0.06976	0.00102	-16.4696	0.2407914	d5v5splin

IWS	um/sec	voltage	distance	gradient	lead pts	end pts
600	16.368	v	d	100	21	18
0	0	v2	d2	100	11	7
800	168.13	v3	d3	100		
500	5.0844	v4	d4	75	12	8
600	16.368	v5	d5	75	13	14



Schematic Apparatus for Phase Diagram Data Determination