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FINAL REPORT

**On: CHARACTERIZATION OF CONVECTION
RELATED DEFECTS IN II-VI COMPOUND
SEMICONDUCTORS**

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SUMMARY

The research carried out under NAG8-913, "Characterization of Convection Related Defects in II-VI Compound Semiconductors", was aimed at exploration of the potential of axial magnetic fields for melt stabilization when applied in Bridgman geometry to growth of HgMnTe. The thrust of the work was directed at the experimental establishment of the limits of magnetic melt stabilization during crystal growth and at the analytical verification of the effects of stabilization on critical materials properties.

The data obtained indicate noticeable stabilization effects, particularly as far as the formation of microscopic compositional inhomogeneities is concerned. The effects of magnetic fields on precipitate formation are found to be minor.

Magnetic field effects were investigated for both "Bridgman" and "Travelling Heater" geometries.

The research was conducted by Dr. P. Becla during the period from May 22 to September 30, 1992.

Magnetic stabilization in vertical Bridgman growth of HgMnTe

Fluid dynamic considerations suggest that during vertical Bridgman growth of pseudo-binary semiconducting alloys, the intensity of convective mixing in the melt is controlled by the balance of two buoyancy forces: the destabilizing thermal gradient, associated with heat input and extraction from the charge; and the axially-stabilizing solute gradients associated with the segregation, (e.g the incorporation of lighter MnTe into the solid and rejection of the more dense HgTe into the melt) at the solidification front. The interaction of these two fields and the large difference between diffusivities of heat and mass result in significant weakening of mixing in the melt, while at the same time promoting another unsteady recirculating structure close to the growth interface¹⁻⁴. The two centro-symmetric circulating flow zones have important consequences on the axial and radial composition uniformity in all II-VI pseudo-binary compounds. Convective flows in the low-intensity zone are usually much weaker than in the upper zone, but they have a complex multi-cellular structure that becomes unsteady at high values of the Grashoff number.² Theoretical calculations predict periodic instabilities in both flow velocity and composition (density). In the pseudo-binary HgMnTe alloys these instabilities are manifest as radial compositional inhomogeneities. It should be noted that the pseudo-binary systems behave differently from the binary and lightly-doped systems. In binary system the convection in the melt is weak enough to permit a solute boundary layer in front of the growth surface. In such systems the traditional diffusion-controlled model can be used.³

The application of magnetic fields to growth of semiconductors leads to a reduction of convective flow intensity in the melt through generation of dissipating Lorentz forces⁵. Growth of HgCdTe and HgZnTe in the presence of 0.2-0.5 tesla transverse fields has been previously reported by Su et al.⁵. Their results indicated that, in the

presence of magnetic field, the asymmetry of the composition in studied wafers was significantly reduced. Our recent experimental results on growth of HgMnTe crystals by the vertical Bridgman method in the presence of applied vertical magnetic field of 3 tesla, showed that both the axial and radial composition nonuniformities can be significantly improved¹. In our experiments the HgMnTe charges were prepared from 99.9999 % pure elemental constituents with an x value of 0.11; they were loaded into the fused-silica tubes of 16 mm ID, subsequently evacuated and sealed. Typical charge length was about 60 mm. The growth furnace used consisted of two 23 cm isothermal zones (employing heat pipes) separated by a 3.5 cm gradient zone. An axial gradient of 50 °C/cm was established in the gradient zone. The furnace assembly was placed inside the 12-inch superconducting magnet capable of generating vertical magnetic fields of up to 3 tesla. The charge lowering rate was about 2 mm/hr. After growth, the ingot was sliced longitudinally and perpendicularly. Microprobe analysis, electroreflectivity, and optical transmission were used for compositional analysis.

Using the conventional vertical Bridgman technique, Fig. 1 shows typical results of the axial and radial composition of Mn in $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ ingots. As the overall electro-optical quality of this material is largely controlled by the uniformity of Mn concentration, Fig.1 reflects the present state-of-the-art materials. A large compositional gradient in the axial direction and compositional variations in the radial direction, induced by significant convection, make this material not acceptable for detector array application. Results of crystals grown in the presence of an applied axial magnetic field are shown in Fig. 2. During crystal growth an axial magnetic field of 3 tesla was turned on and off periodically at time intervals of 12 hrs. The results clearly indicate that growth in the presence of an axial magnetic fields produces materials with much more uniform radial composition than materials grown in the absence of a magnetic field. Improvements in the axial direction were less pronounced. The limited

improvement in axial composition uniformity is attributed to the short length of the charge used. A comparison of the detailed structure of radial composition in conventional and magnetically grown materials, obtained by electroreflectivity measurements, is shown in Fig. 3. Results reveal the presence of an irregular microsegregation structure in the conventionally grown material which is strongly reduced for growth in a magnetically stabilized melt. These results clearly demonstrate that an applied magnetic field significantly improves the compositional uniformity and can be useful in the production of high-quality pseudo-binary HgMnTe alloys.

Traveling heater method

The traveling heater method (THM) was developed by Wolf⁶. This solution growth technique has been applied to many binary and pseudobinary semiconductor and semimetal compounds.⁷⁻¹⁰ Growth takes place at a relatively low temperature, thereby reducing complications related to material properties such as high vapor pressure at the melting point, high segregation coefficient, etc. THM is based on forcing a narrow molten zone of solution through a solid ingot; during the slow movement of the liquid zone, dissolution occurs at the top and re-crystallization at the bottom. The main advantage of this growth process is a significant improvement in defect density, impurity concentration, and compositional homogeneity. Maintaining the molten zone at a constant narrow dimension significantly reduces problems associated with high Hg vapor pressure, convective melt flow, and contamination. Low-temperature solution growth also has some disadvantages, primarily the formation of precipitates which can be reduced by selecting extremely low movement of the molten zone. Typical growth rates used in THM are on the order of 1-2 mm per day, which is more than one order of magnitude lower than in Bridgman growth. Additional complications arise from the requirements of macroscopically very homogeneous feed material and the stability of

the liquid zone temperature field. For growth of the HgMnTe single crystals we adopted a three-zone THM system similar to that used by Colombo for HgCdTe¹⁰. The schematic diagram of this system is shown in Fig.4. It allowed growth of HgMnTe crystals, 16 mm and 22.5 mm in diameter, of $x=0.11$ by single pass processing. Typical data on radial and axial composition profiles in THM-grown HgMnTe crystal are shown in Figs. 5 and 6. Composition uniformity is found to be about 0.03%, over 10 mm, acceptable for detector arrays.

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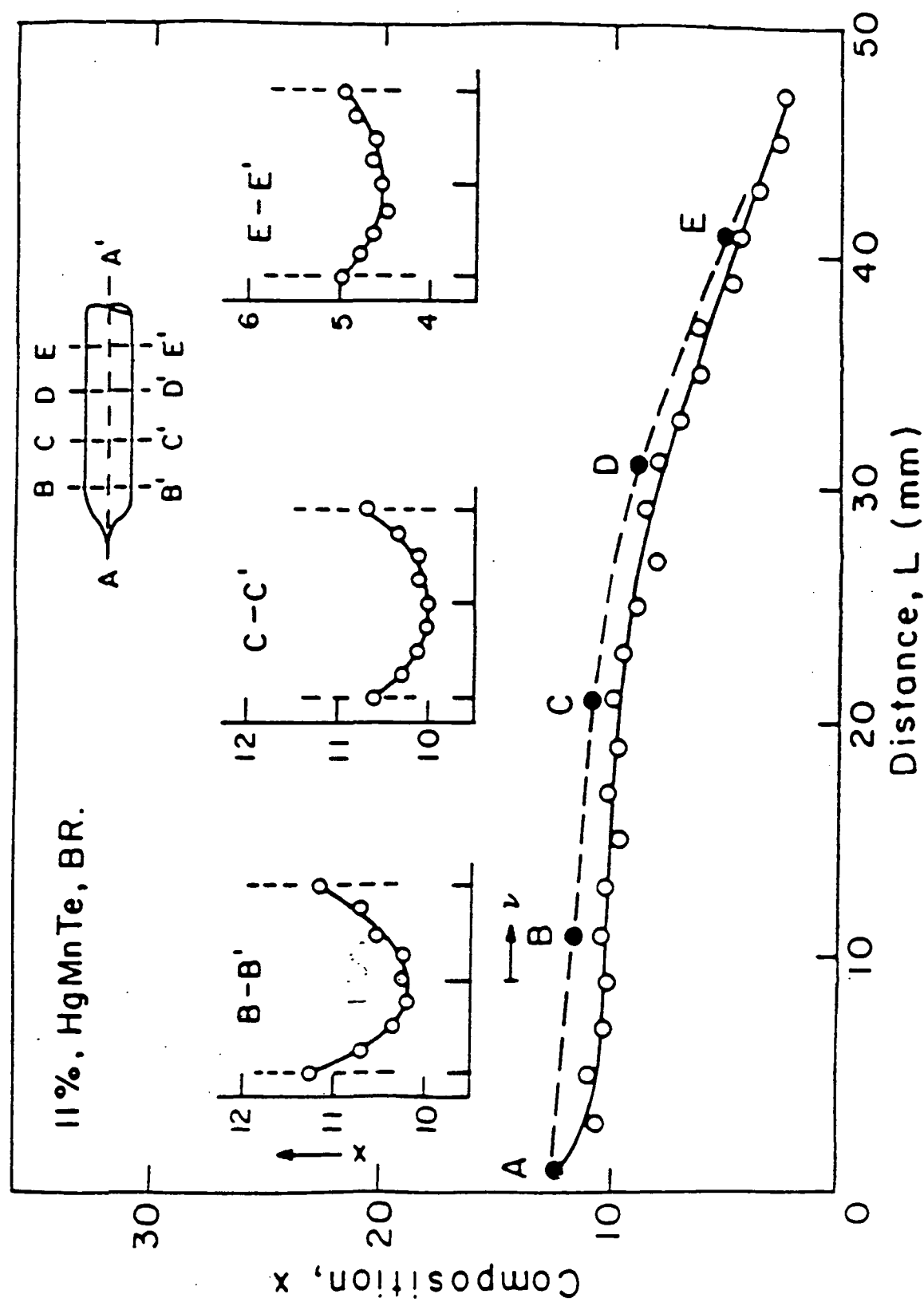


Fig. 1 Radial and longitudinal composition profiles of HgMnTe grown by conventional vertical Bridgman technique.

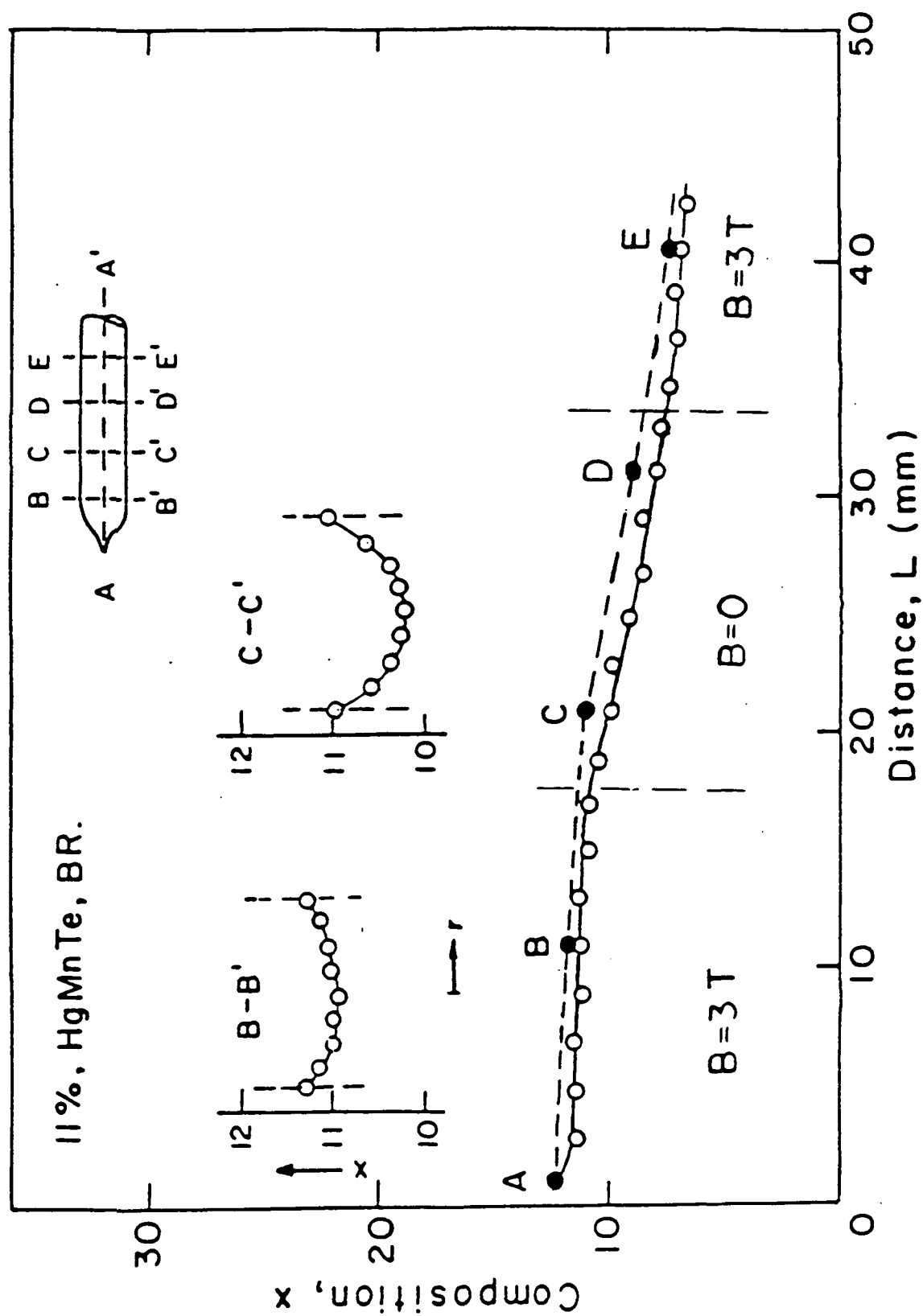
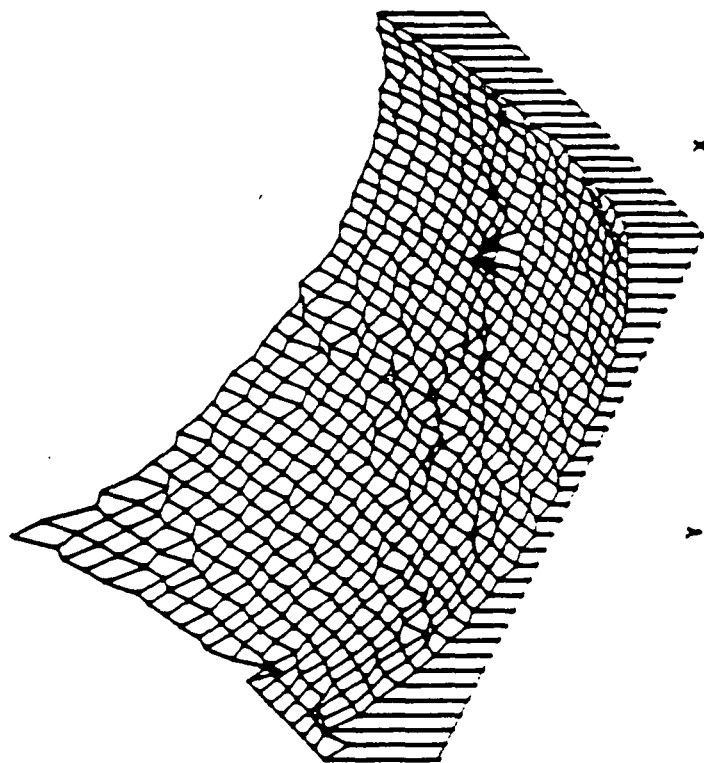
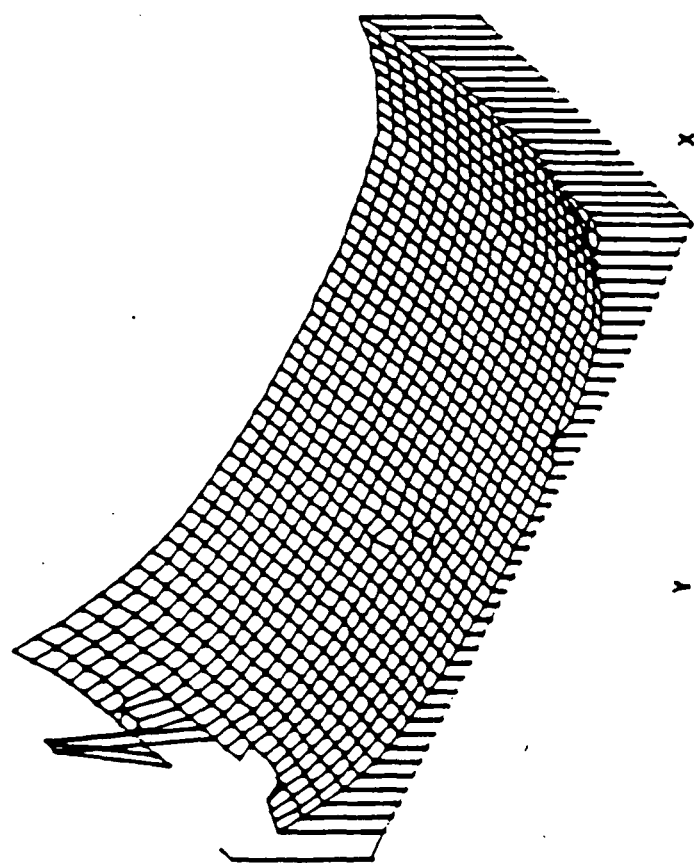


Fig. 2 Radial and longitudinal composition profiles of HgMnTe grown by vertical Bridgman technique with and without magnetic field.

RADIAL DISTRIBUTION OF Mn Electro-reflectivity Measurement.



CONVENTIONAL
BRIDGMAN-GROWN



MAGNETIC
BRIDGMAN-GROWN

Fig. 3 Profile of $E_1 + \Delta$ transition in HgMnTe ($x=0.11$) wafer obtained by electro-reflectivity measurements. Profile reflects the distribution of Mn in HgMnTe wafer grown by (a) conventional Bridgman, (b) magnetic Bridgman.

TRAVELING HEAT METHOD

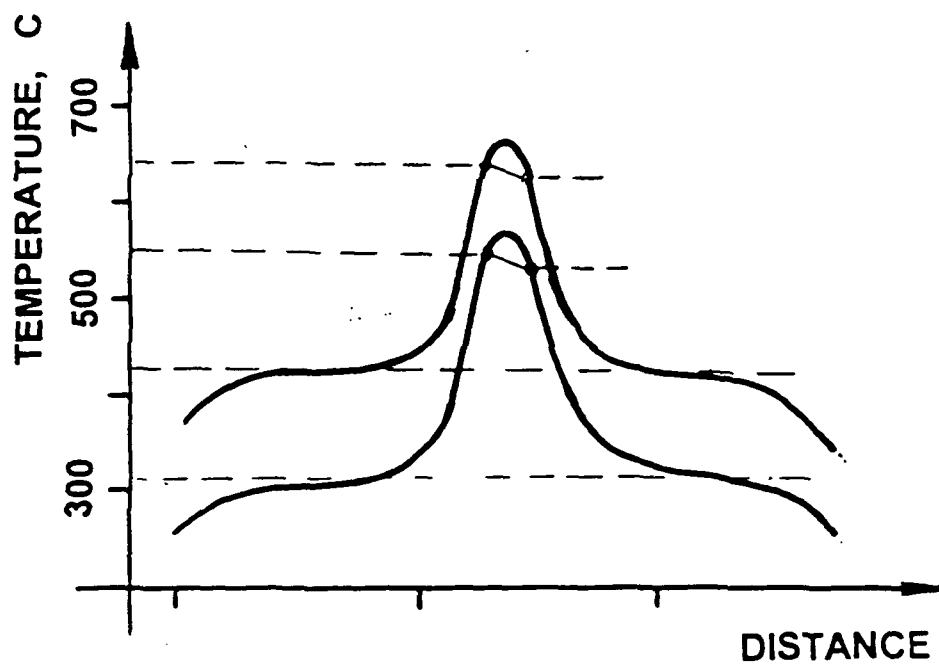
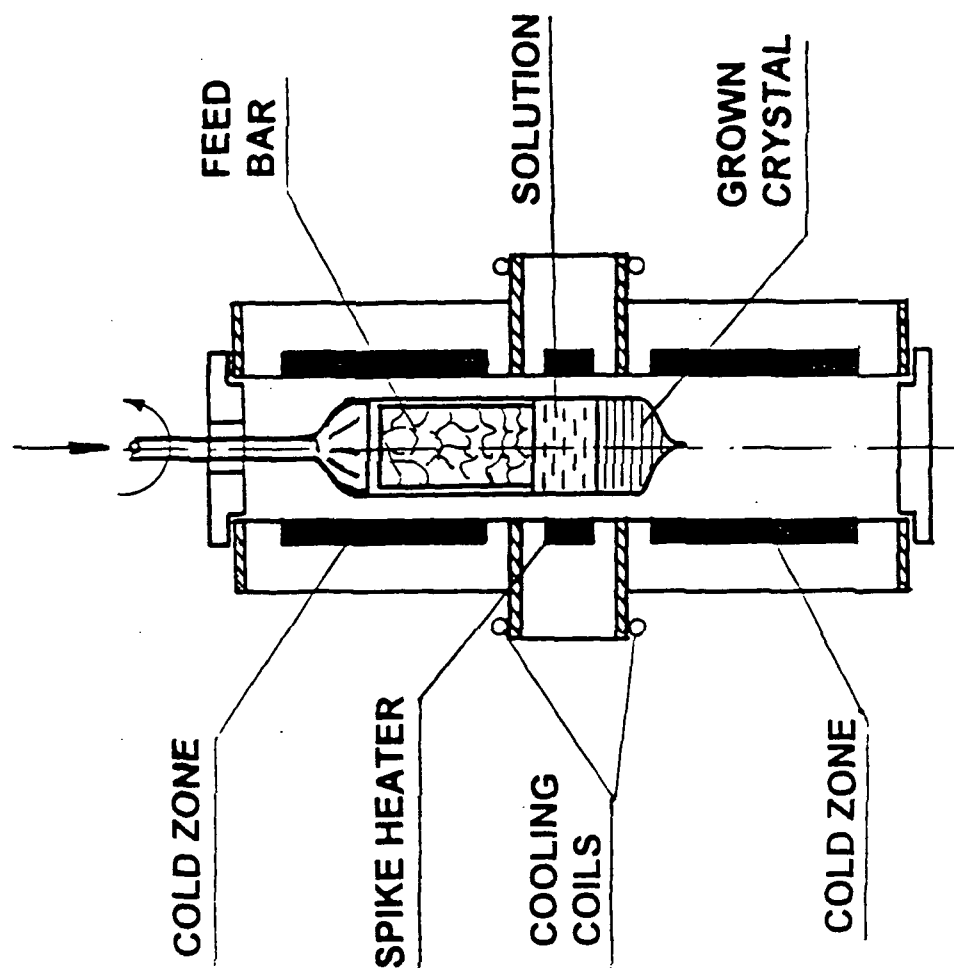


Fig. 4 Schematic diagram of the three zone traveling heater method (THM).

Longitudinal Composition Profile

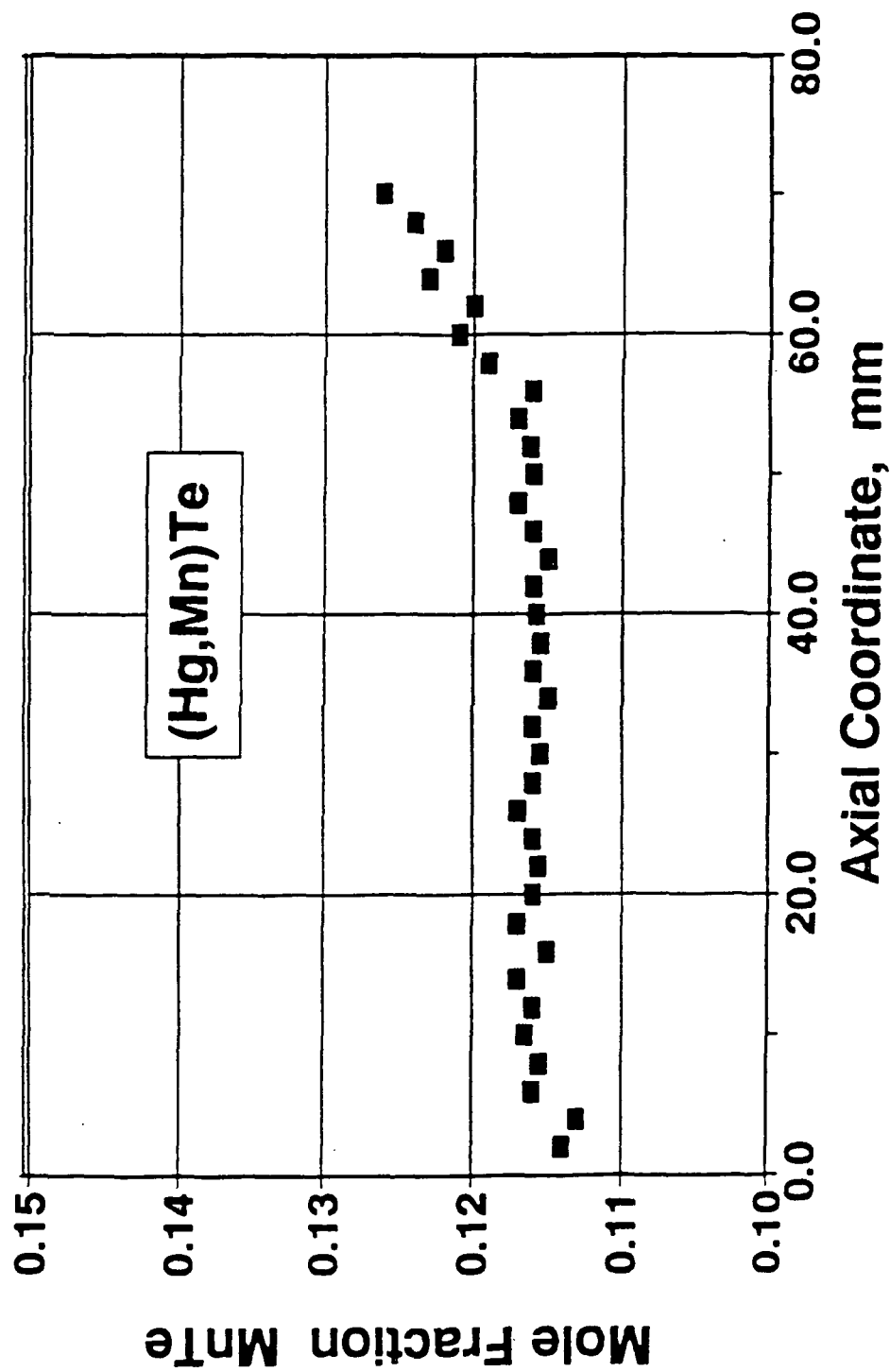


Fig. 5 Longitudinal composition profile of Mn in HgMnTe grown by the traveling heater method.

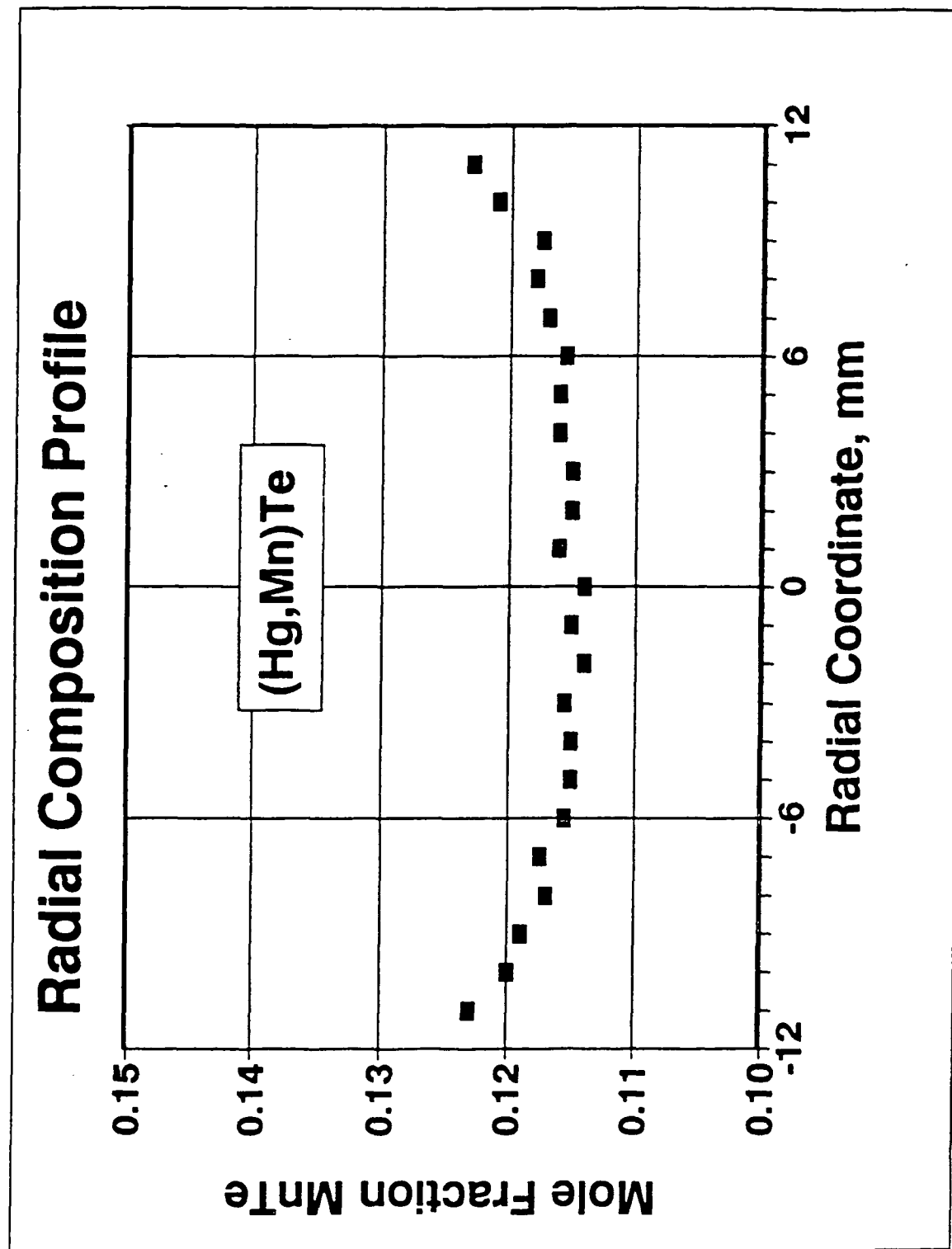


Fig. 6 Radial composition profile of Mn in HgMnTe grown by the traveling heater method.