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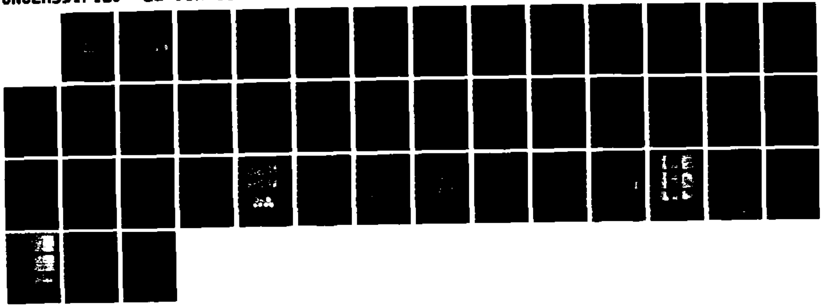

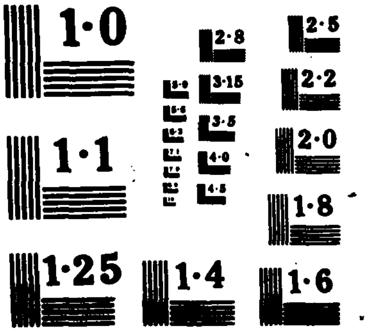
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The thrust of this research project was directed at the development of new approaches leading to growth of CdTe single crystals with improved crystalline and chemical perfection. In pursuit of this objective a theoretical analysis was made of the stability of the growth interface as a function of crystallographic orientation. Using the concept of dangling bond densities, it was found that experimentally observed solitary and lamellar twinning phenomena during growth can be directly

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related to anisotropy in the energetics of unavoidably curved crystal melt interfaces.

The theoretical results obtained led to the development of a vertical Bridgman growth configuration in which heat transfer control is accomplished through an axially aligned heat exchange system comprising a heat pipe, a gradient control zone, and a heat levelling device. The axial thermal characteristics of the system was found to be in excellent agreement with mathematical modelling results. It was found that the critical radial thermal gradient configuration is in a dominant manner controlled by heat transfer along the wall of the charge confining crucible.

As an alternate approach to melt growth of CdTe, the suitability of the high pressure liquid encapsulation Czochralski technique (HP-LEC) was investigated. Using coaxial thermal reflector systems it was possible for the first time to achieve for CdTe a degree of crystalline perfection which exceeds that obtained through conventional Bridgman growth.

In the course of this study, analytical techniques, including IR transmission microscopy with image processing and absorption spectroscopy of the optical band edge, were developed and applied to investigations of the bulk defect structure.

The results obtained during this research program constitute the basis for extensive DARPA, Air Force, and NASA sponsored research on growth of III-V and II-VI compound semiconductor systems.

GROWTH OF CADMIUM TELLURIDE UNDER CONTROLLED HEAT TRANSFER CONDITIONS

Final Report

A.F. Witt

June 1986

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FOREWORD

Property requirements of electronic and opto-electronic materials for device fabrication have until recently not been an issue of primary concern since yield and performance characteristics could in most instances not be related to bulk properties. Critical materials deficiencies in silicon IC fabrication could be overcome as needed through changes in device architecture, device processing, or through resort to epitaxial overgrowth. These approaches, while effective in silicon based large scale device integration, are found largely to be ineffective for very large scale integration.

In recent years the rate of advance in device technology was so high that simultaneous progress made in materials preparation was inadequate to meet emerging, more stringent, property requirements. While deficiencies in properties of the elemental semiconductors are serious, those encountered in compound semiconductors are overwhelming; thus the establishment of a GaAs and InP based device technology and the evolution of a viable industrial II-VI compound semiconductor activity appear at present largely controlled by advances in materials processing. In context it is significant that industrial semiconductor crystal growth, the basis for all of device technology, is as yet virtually devoid of a scientific framework and therefore by necessity conducted on a largely empirical basis. The unavailability of a scientific basis for industrial crystal growth can on the one hand be attributed to turbulent convective interference with heat and mass transport in the melt and on the other hand to complications in the control and quantification of prevailing thermal boundary conditions.

A major deficiency of the currently practiced empiricism in crystal growth lies in our inability to take a generic approach. Expertise gained in analog systems is not readily transferable; results obtained in one laboratory under a certain set of conditions are not necessarily comparable with those obtained elsewhere under apparently identical conditions.

The presently reported effort was aimed at: (a) establishing at MIT experimental capabilities for growth of CdTe, (b) broadening the science base of melt growth of semiconductors, (c) establishing stability criteria for Bridgman type growth of CdTe, and (d) explore the potential of the LEC technique with heat and mass transport control for growth of CdTe. Although the research was focused on growth and characterization of a specific material, the approach taken was largely generic, with the results being consequential to other materials such as GaAs and InP as well. Thus major segments of DARPA, Air Force, and NASA sponsored research were affected by results of the investigation and in part were redirected as a result. Data and insight gained from this study are considered major contributions to the understanding of semiconductor crystal growth. The primary benefit, however, is likely derived from the realization that needed advances in processing science and technology require interdisciplinary, interdepartmental approaches leading to the replacement of empirical procedures by expert systems with steadily increasing elements of artificial intelligence.

CONTENTS

Foreword....................................2

List of Illustrations.......................6

Research Report.............................8

  Problem Definition........................8

  Summary of Significant Research Results...9

  List of Publications and Technical Reports Published....................15

  List of Participating Scientific Personnel and Associated Degree Earned.........16

Bibliography...............................17

Appendixes: Figures........................29

LIST OF ILLUSTRATIONS

Fig. 1 CdTe grown with heat transfer control in a vertical Bridgman configuration; non-twinned region generally extends a 3 to 4 cm crystal length. Dislocation density as determined from etch pit counts ranges in average from $5x10^3$ to about $5x10^4$ cm^{-2}.

Fig. 2 Growth interface relocation, unavoidable in conventional Bridgman configuration, due to thermal end effects. Significant is the sensitivity of the growth rate behavior, which deviates significantly from the ampoule lowering rate, to the placement of the control thermocouple (T, B, top and bottom of ampoule in original position) and the mode of heat extraction from the ampoule (Indirect and Direct cooling).

Fig. 3 Stability map against twinning for CdTe. The figure provides for a (001) seeded crystal a density of dangling bonds composite surface and all of its first-order twins in a projection of the three-dimensional surface onto the {001} surface.

Fig. 4 Configuration of smallest (8 atom cluster) which can function as nucleus for twin formation. Notice the average of 1.75 dangling bonds per atom.

Fig. 5 Stability region (cross hatched) against twinning in thermal gradient (G) vs. growth rate (R) space, as predicted by the melt clustering model.

Fig. 6 Schematic of the axial temperature distribution in the CdTe charge and the confining crucible near the growth interface. Notice that the inequality of the k_L and k_S mandates a radial temperature gradient in confined charges.

Fig. 7 Growth interface shape for CdTe as a function of its position within the gradient zone of the heat controlled vertical Bridgman system; it should be noticed that the sensitivity of the interface morphology to its axial position is lost upon confinement by a crucible.

Fig. 8 CdTe grown by the high pressure (450 psig) LEC technique. Wafers cut from the crystal indicate initial growth with a limited number of lamellar twins and deterioration of conditions upon reseeding in the lower segment.

Fig. 9	Optical band edges for CdTe and CdMnTe (20 wt% Mn) as obtained by the spectra-scan system. The developed procedure permits compositional analyses with 15 µm spatial resolution.
Fig. 10	Optical band edge characteristics for CdTe grown by the vertical Bridgman technique and by HP-LEC
Fig. 11	Micrograph of TEM analysis for CdTe prepared for electron transparency by ion-milling. (The massive defect formation observed throughout is absent in specimen prepared by wet jet etching.)
Fig. 12	HEED micrograph of CdTe grown by the Bridgman technique; streak formation is taken to be indicative for the presence of atomically thin lamellar precipitates.

RESEARCH REPORT

PROBLEM DEFINITION

This research program on single crystal growth of CdTe was directed at:

- The establishment of causes for failure to achieve or even approach theoretical degrees of crystalline and chemical perfection in CdTe and related II-VI compound semiconductors.
- The development of science based experimental growth procedures yielding crystal perfection which meets property requirements for device fabrication.

CdTe and related compounds constitute primary matrix materials for IR focal plane arrays and discrete detectors. The material, obtained exclusively by Bridgman type crystal growth, is characterized by a very low degree of crystalline perfection; it exhibits precipitates, lamellar and solitary twinning as well as low angle grain boundaries, the result of excessively high densities of dislocations. Efforts to obtain single crystal of improved crystalline perfection through growth by the LEC technique have been even less successful. Attempts to achieve device material by epitaxial approaches including LPE, CVD and MBE failed so far because of the unavailability of adequate substrate material.

The presently reported research effort focussed on:

- Growth of CdTe with heat transfer control in vertical Bridgman configuration.
- Exploration of LEC growth of CdTe.
- The identification of growth characteristics associated with the conventional vertical Bridgman-type configuration making use of current induced crystal-melt interface demarcation and differential chemical etching.
- The development of theoretical approaches aimed at the establishment of a scientific framework for the generation of lamellar and solitary twins, grain boundaries, and dislocations during growth under defined boundary and growth conditions.
- The determination of orientation dependent stability criteria for the crystal-melt interface.
- Development of advanced approaches to melt growth of CdTe.

SUMMARY OF SIGNIFICANT RESEARCH RESULTS

Bridgman Growth

- Using a vertical, seeded Bridgman configuration with heat pipe based axial and radial thermal gradient control it was possible to grow (at 20% yield) twin and grain boundary free CdTe of 1.2 cm diameter and a length of up to 3 cm with an average dislocation density of about $2 \times 10^4/cm^2$;

twinned, grain boundary free single crystals were grown at a yield of better than 60% (Fig. 1).

- Deficiencies of conventional Bridgman growth were identified as thermal endeffects (due to growth geometry) giving rise to continuously varying thermal gradients and consequently to transients in growth rate and growth interface morphology (Fig. 2).
- Contrary to predictions, it was found that the perfection of CdTe grown in vertical Bridgman configuration is not noticeably affected by the chemical nature of the confining crucible material; graphitization, total liquid encapsulation by B_2O_3 and the use of a boron-nitride insert in quartz ampoules yielded virtually the same crystal perfection during growth under otherwise comparable conditions.
- A theoretical analysis of growth stability based on the orientation-dependent dangling bond density concept was made. It indicates that twin formation is one mode of stabilization for non-planar crystal-melt interfaces: The theory accounts for the increased twinning tendency of all 'A' seeded polar crystals (III-V and II-VI compound semiconductors) as a consequence of low dangling bond density in that crystallographic orientation; the theory provided explicit stability maps for elementary semiconductors (Fig. 8).
- The developed dangling bond model indicates that the favored growth direction in unseeded vertical Bridgman growth is the direction which exposes the higher density of dangling bonds to the melt; twinning operations in all instances will expose surface orientations with increased

dangling bond density: most stable growth in CdTe is the <111>B direction; growth stability is sensitive to both the axial and radial thermal field distribution; it is also sensitive to the rate of growth which is not to exceed a maximum value.

- Based on the experimentally proven existence of associated species in CdTe melt, a clustering model was developed. The results indicate that the smallest cluster of relative stability capable of nucleating oblique twins comprises eight atoms; the theory predicts that cluster formation is favored by slow rates of growth and by low thermal gradients (Figs. 4 and 5).
- The heat transfer for CdTe growth in vertical Bridgman configuration was modelled. Analyzing the heat pipe operated three-zone system used in the present research effort, it is found that the control of the growth interface morphology through its positioning within the gradient zone is severely impeded by the 'interface effect': the undesirable axial flow of heat within the confining crucible material. The theoretical study, confirmed by experiment, shows that needed control over the shape of the crystal-melt interface is contingent on the development of confinement systems that are chemically compatible with the charge, have adequate mechanical strength, and will not imbalance axial heat flow within the growth crystal (Figs. 6 and 7).

Liquid Encapsulated Czochralski Growth

- Using a pre-cast charge (5N, II-VI, Inc.) and B_2O_3 (Pasa Type D) as encapsulant it was possible to grow at 450 psi over-pressure and a growth rate of 4 μm/s CdTe crystals of up to 15 mm diameter which contained a limited number of lamellar twins and was devoid of grain boundaries and optically visible precipitates (Fig. 8).

* It was found that B_2O_3, exhibiiting incomplete wetting in contact with solid CdTe, is an inadequate charge encapsulant. The non-wetting condition is found to result in evaporative Cd losses from the melt (loss of stoichiometry) and from the growing solid (generation of point defects after growth).

* Enhanced wetting of the growing crystal by the liquid encapsulant was pursued through the temperature dependence of the viscosity of the encapsulant and the modifications of chemical and optical properties of B_2O_3 through the addition of other glass forming oxides, notably SiO_2.

* All attempts to grow CdTe by the low pressure LEC technique (at pressures up to 4.5 atm) failed, primarily because of excessive evaporative losses from the melt along the perimeter of the crystal-encapsulant boundary.

* A thermo-elastic stress analysis was made for CdTe growth in the LP-LEC configuration. It was found that the maximum allowable heat flux (loss) from the crystal surface to the environment, for which the resulting radial thermal gradients yield stresses which do not exceed CRSS, is only 1/140 that of silicon. The development of a viable LEC approach to growth of CdTe is found to be contingent on effective melt encapsulation and on heat loss control.

Characterization of CdTe

- Making use of a spectra scan 'IR spectrometric camera', a technique was developed which allows the virtually instantaneous determination of optical band edge characteristics for CdTe and related compounds. In a scanning mode the spectrometer could provide radial compositional analyses of CdMnTe with a precision of better than ±1%; the system was also successfully applied to the differentiation of Bridgman and Czochralski type materials, based on characteristic differences in the optical band edge behavior Figs. 9 and 10).
- In conjunction with TEM and STEM analyses of bulk defects, different techniques were investigated for preparation of electron transparent CdTe specimens. Both ion-milling and plasma etching were found to introduce bulk defects during wafer preparation. An automated wet jet etching technique with feedback control was developed and found to yield reproducible results without artifacts (Figs. 11 and 12).

The presently reported research effort has implications which transcend the domain of CdTe growth. It contributed substantially to the development of a quantifiable, computer controlled Bridgman type system, now extensively used in research on non-man-tended growth of semiconductors in reduced gravity environment. This research, moreover, was instrumental in the realization of a CCD based thermal imaging system, considered essential for the advancement of the LEC technique as it applies to growth of GaAs and InP.

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2. Reentrant Edge Growth Mechanism
3. Twinning Crystallography
4. Ribbons, Dendrites, Whiskers
5. Etching
6. Defects Associated with Twinning
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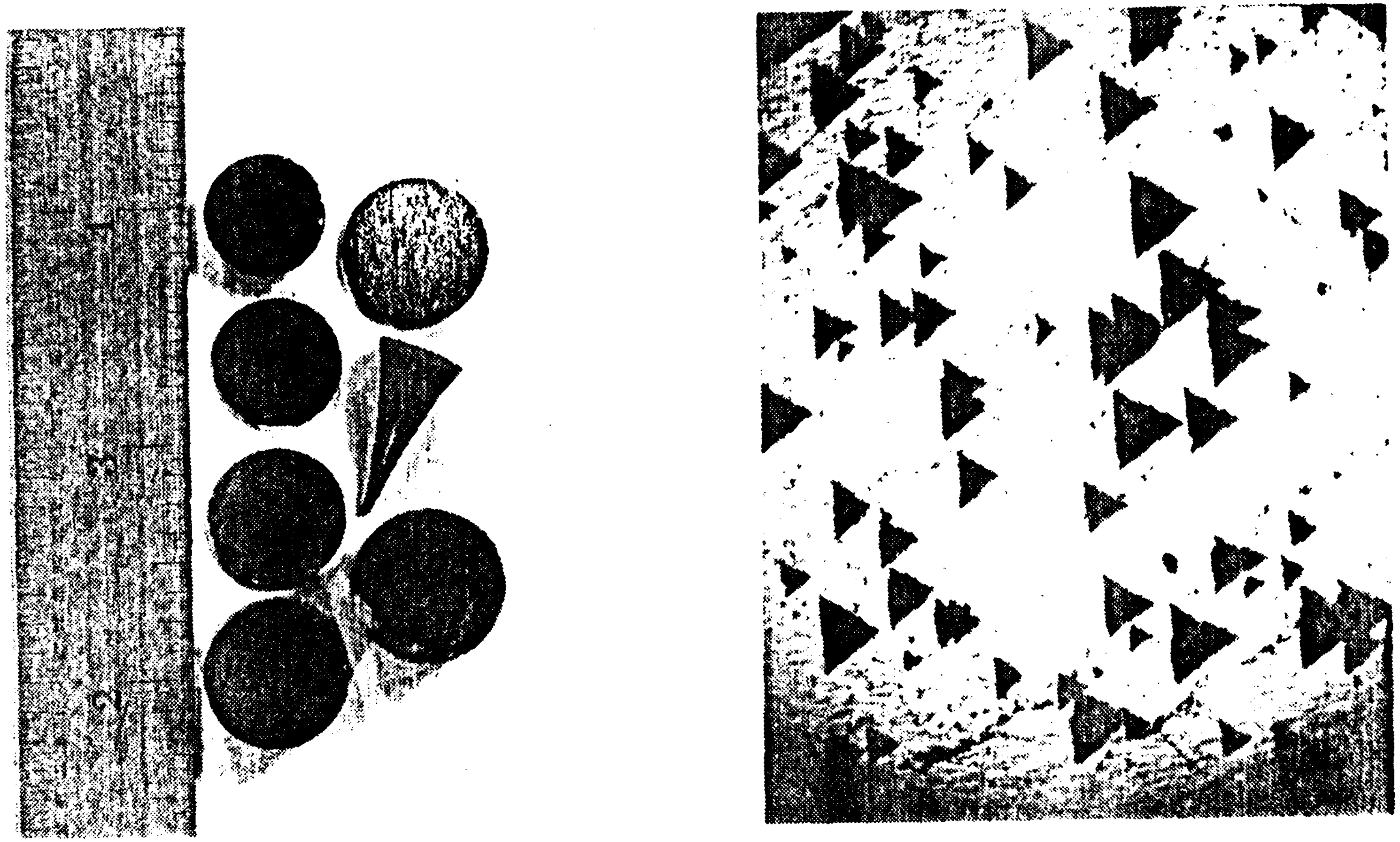


Fig. 1

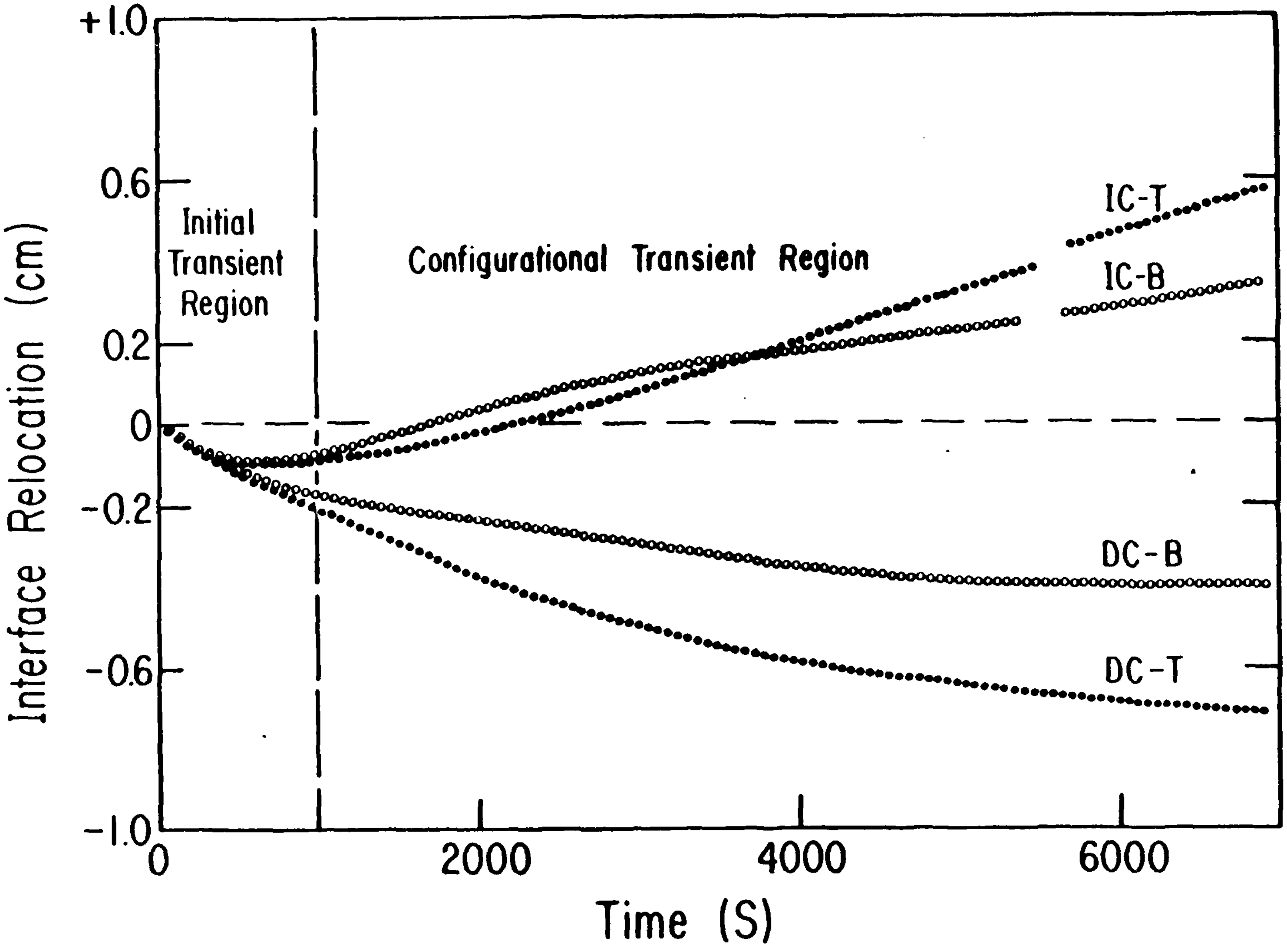
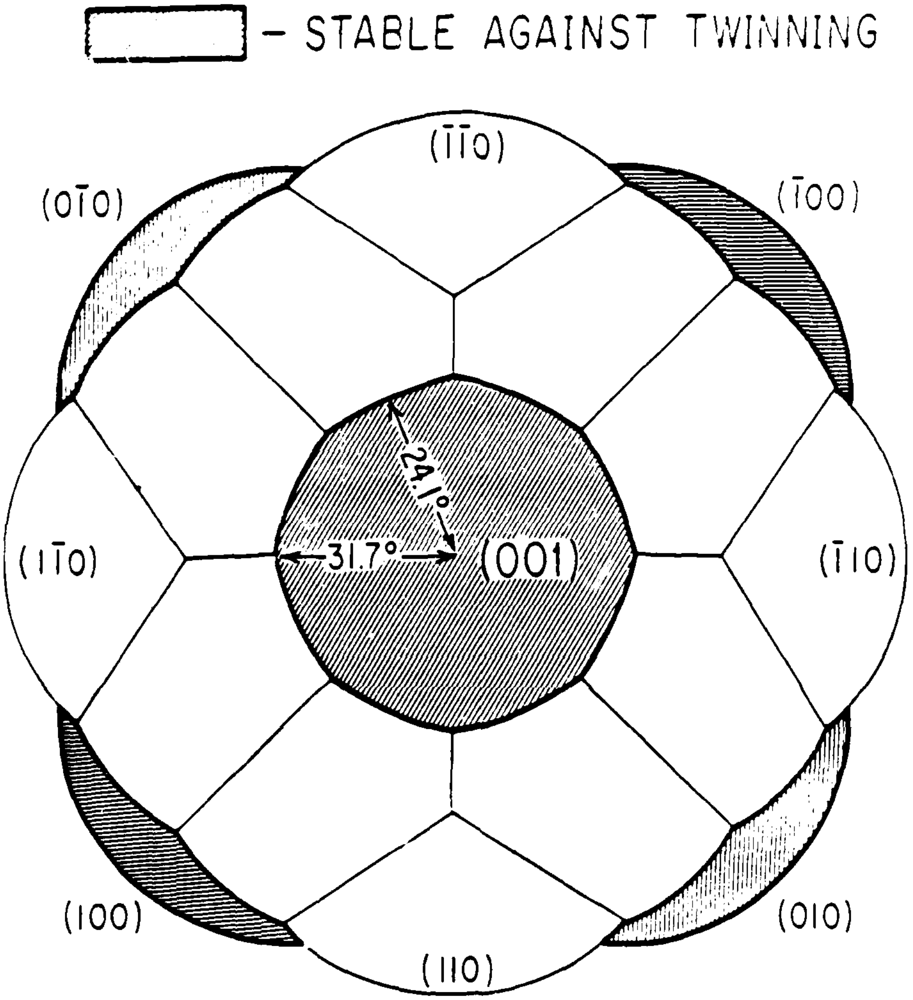

+1.0
0.6
0.2
0
-0.2
-0.6
-1.0
Interface Relocation (cm)
0
2000
4000
6000
Time (S)
Initial
Transient
Region
Configurational Transient Region
IC-T
IC-B
DC-B
DC-T

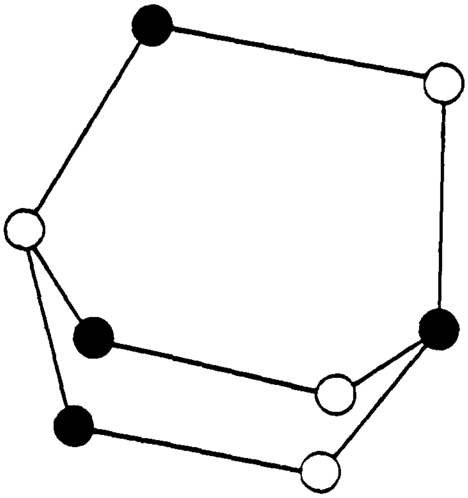
Fig. 2



DANGLING BOND DENSITY VS. ORIENTATION
Composite for all first order twins

Fig. 3

8-ATOM CLUSTER



Average no. of dangling bonds per atom is 1.75

Fig. 4

Prediction of 8-atom clustering model for single crystal growth

$$GR > V\Delta Tu \frac{\delta^2 N_\infty}{\delta t \delta V}$$ (No clusters)

$$\frac{G}{R} > m' \frac{C_\infty}{D} \frac{1-k_0}{k_0}$$ (No constitutional supercooling)

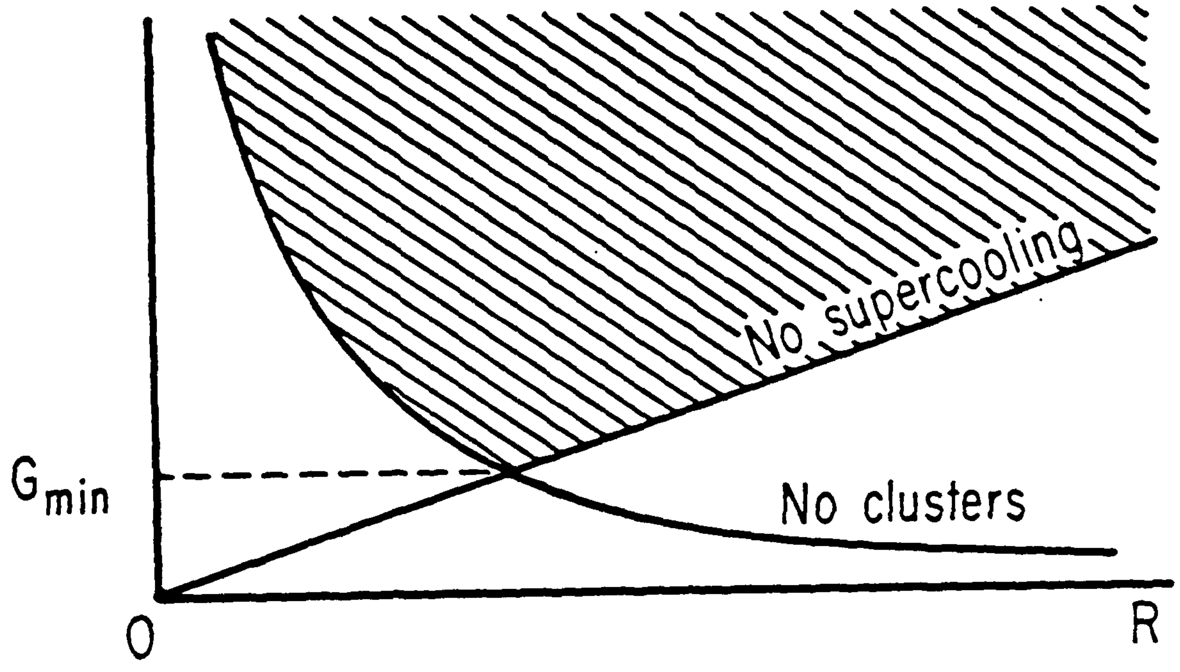


Fig. 5

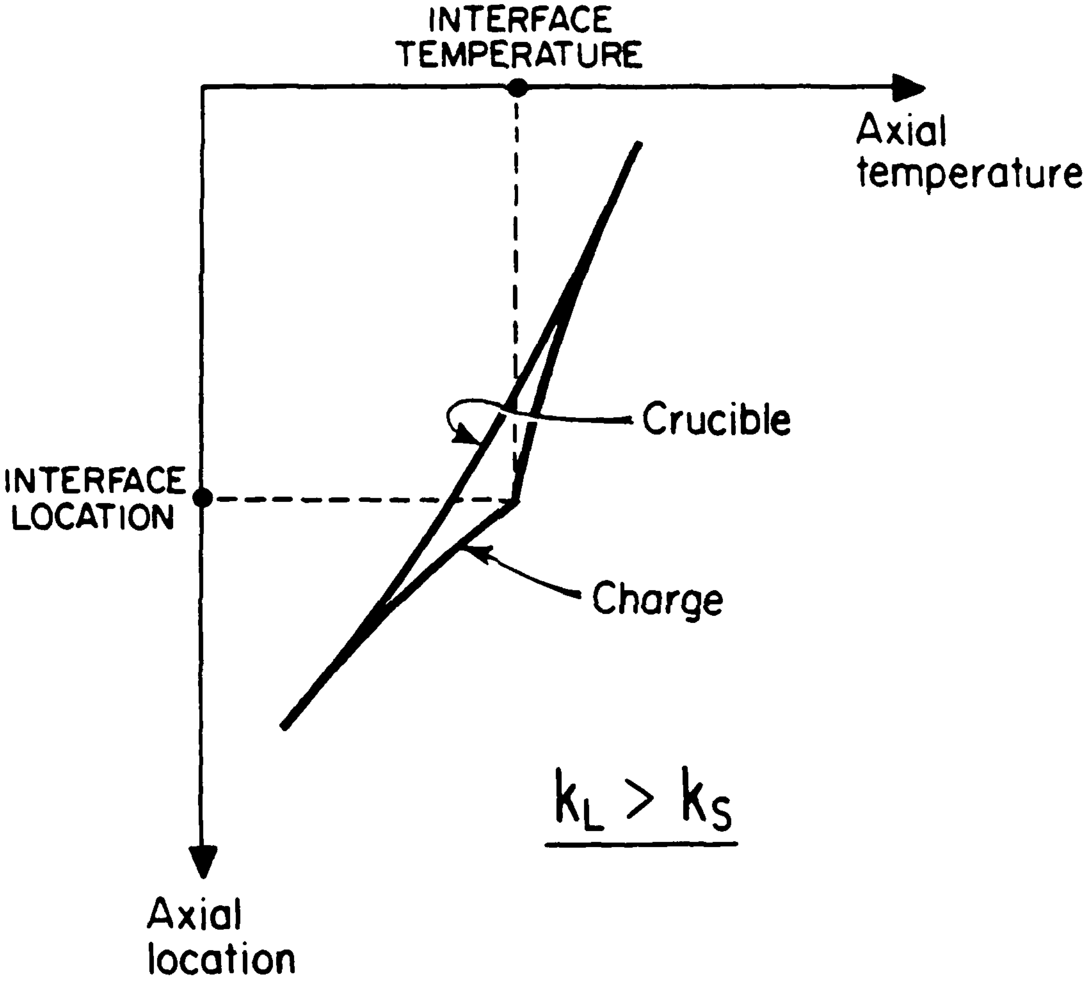

INTERFACE TEMPERATURE
Axial temperature
Crucible
INTERFACE LOCATION
Charge
$k_L > k_S$
Axial location

Fig. 6

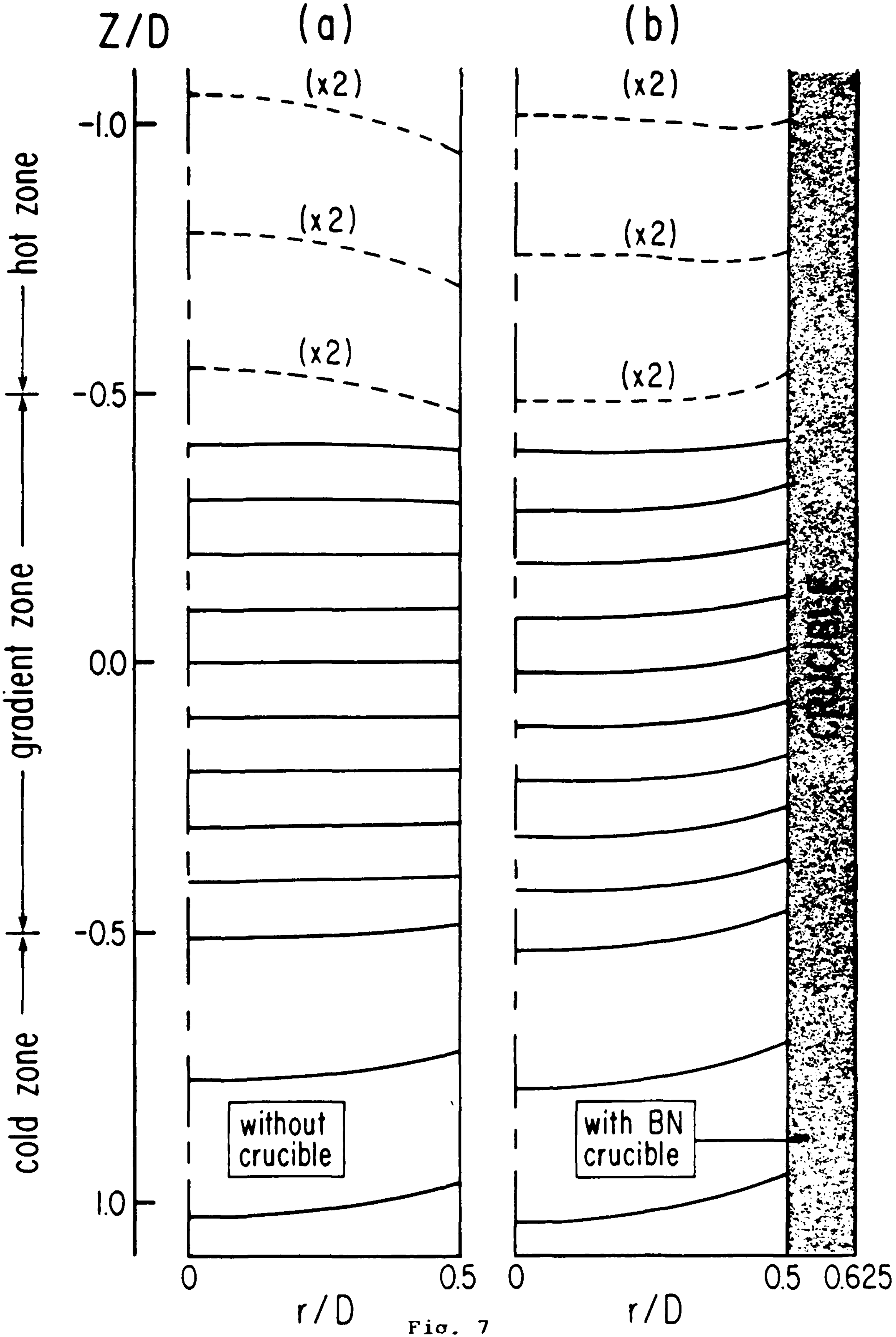

Z/D
(a)
(b)
(x2)
(x2)
(x2)
(x2)
(x2)
(x2)
-1.0
-0.5
0.0
-0.5
1.0
hot zone
gradient zone
cold zone
without crucible
with BN crucible
CRUCIBLE
0
0.5
0
0.5
0.625
r/D
r/D

Fig. 7

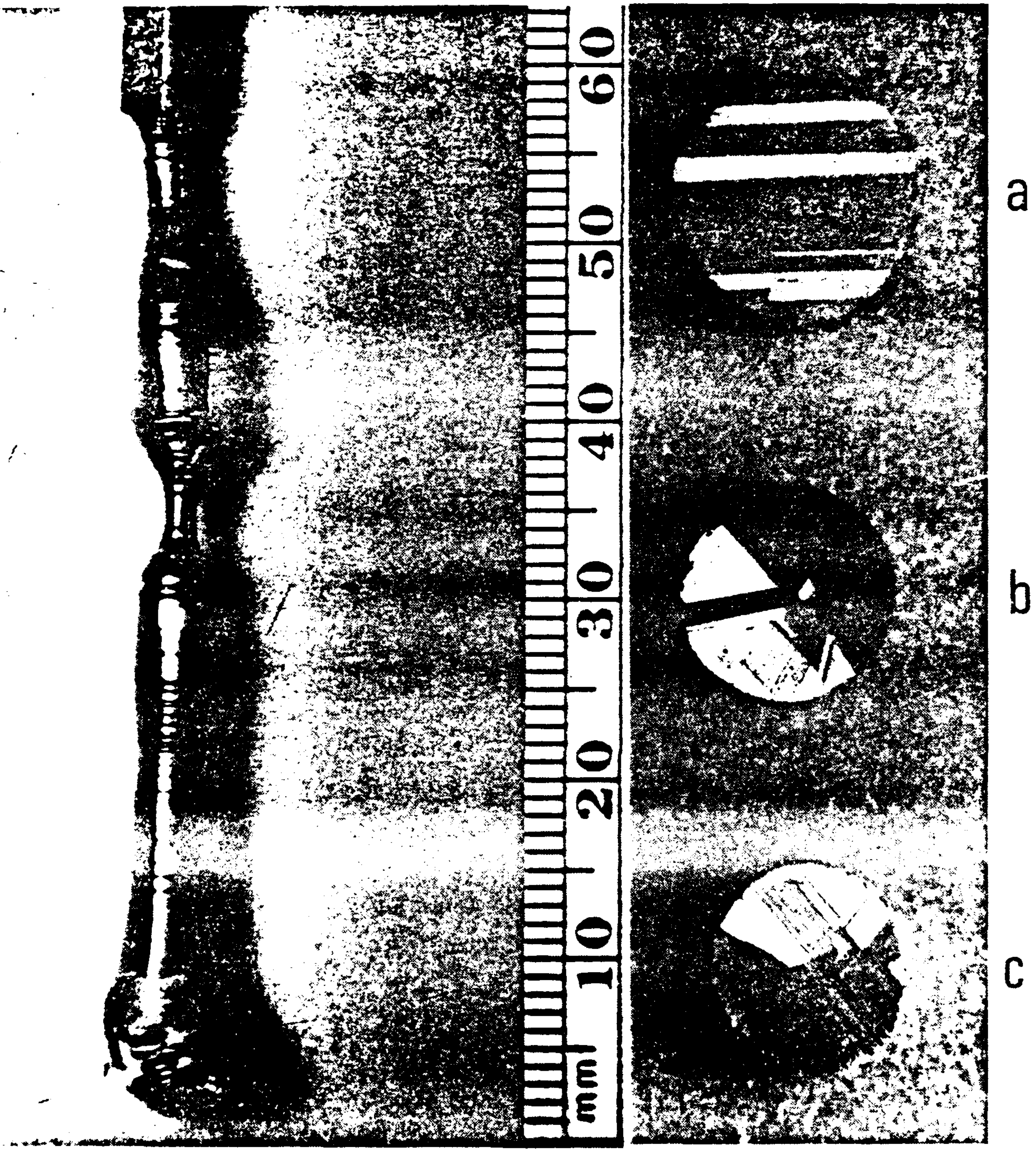


Fig. 8

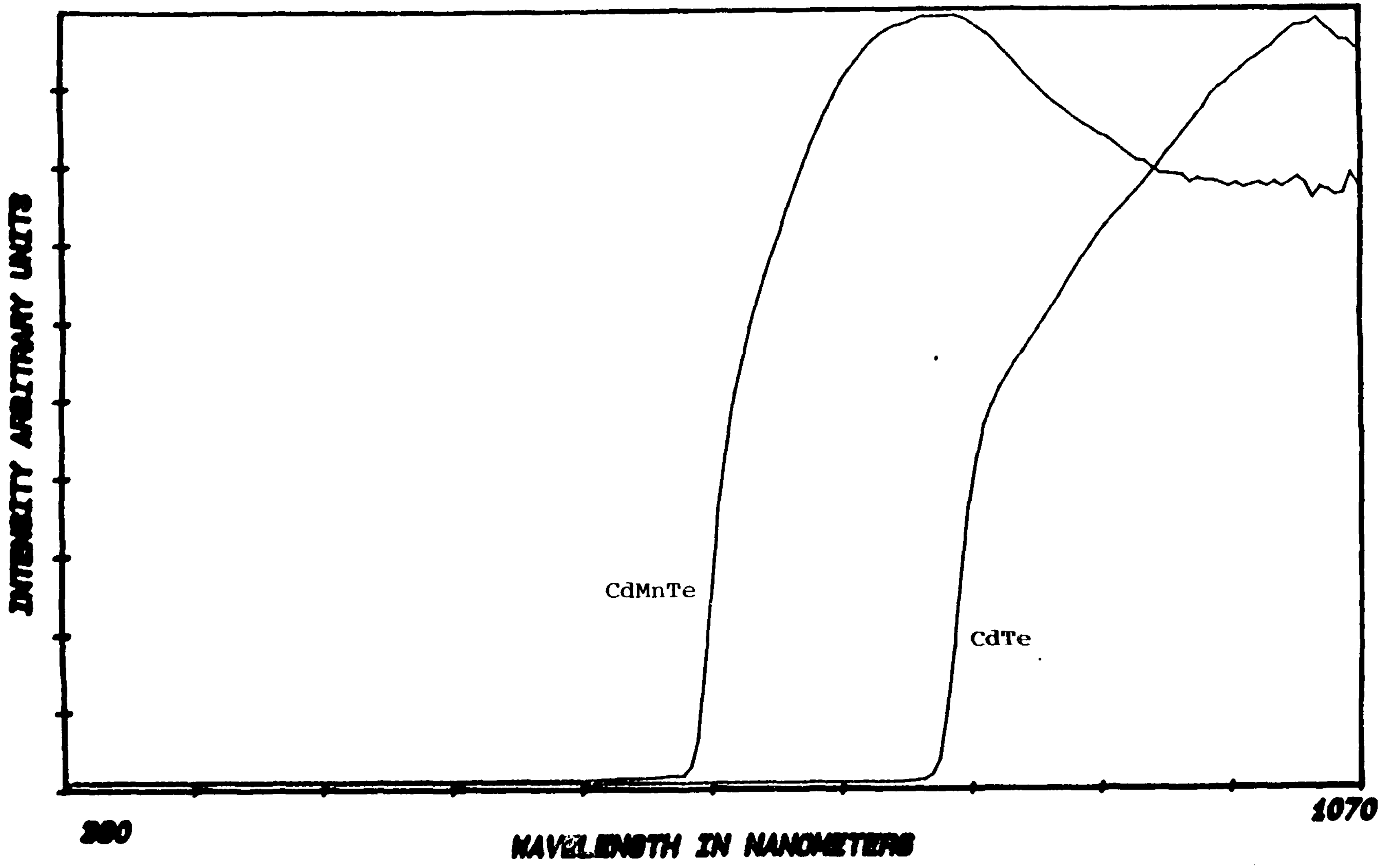

INTENSITY ARBITRARY UNITS
WAVELENGTH IN NANOMETERS
200
1070
CdMnTe
CdTe

Fig. 9

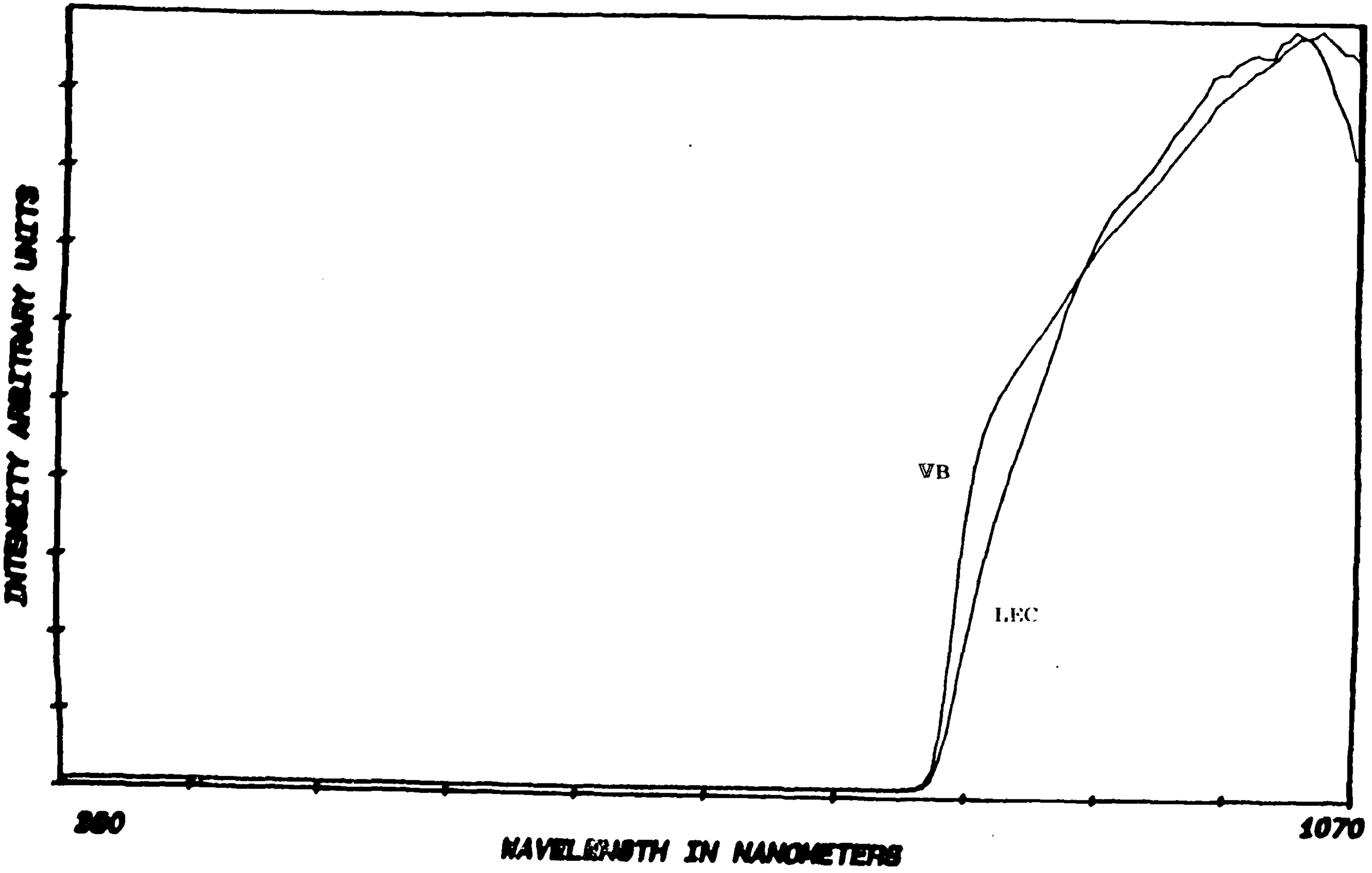

INTENSITY ARBITRARY UNITS
VB
LEC
380
1070
WAVELENGTH IN NANOMETERS

Fig. 10

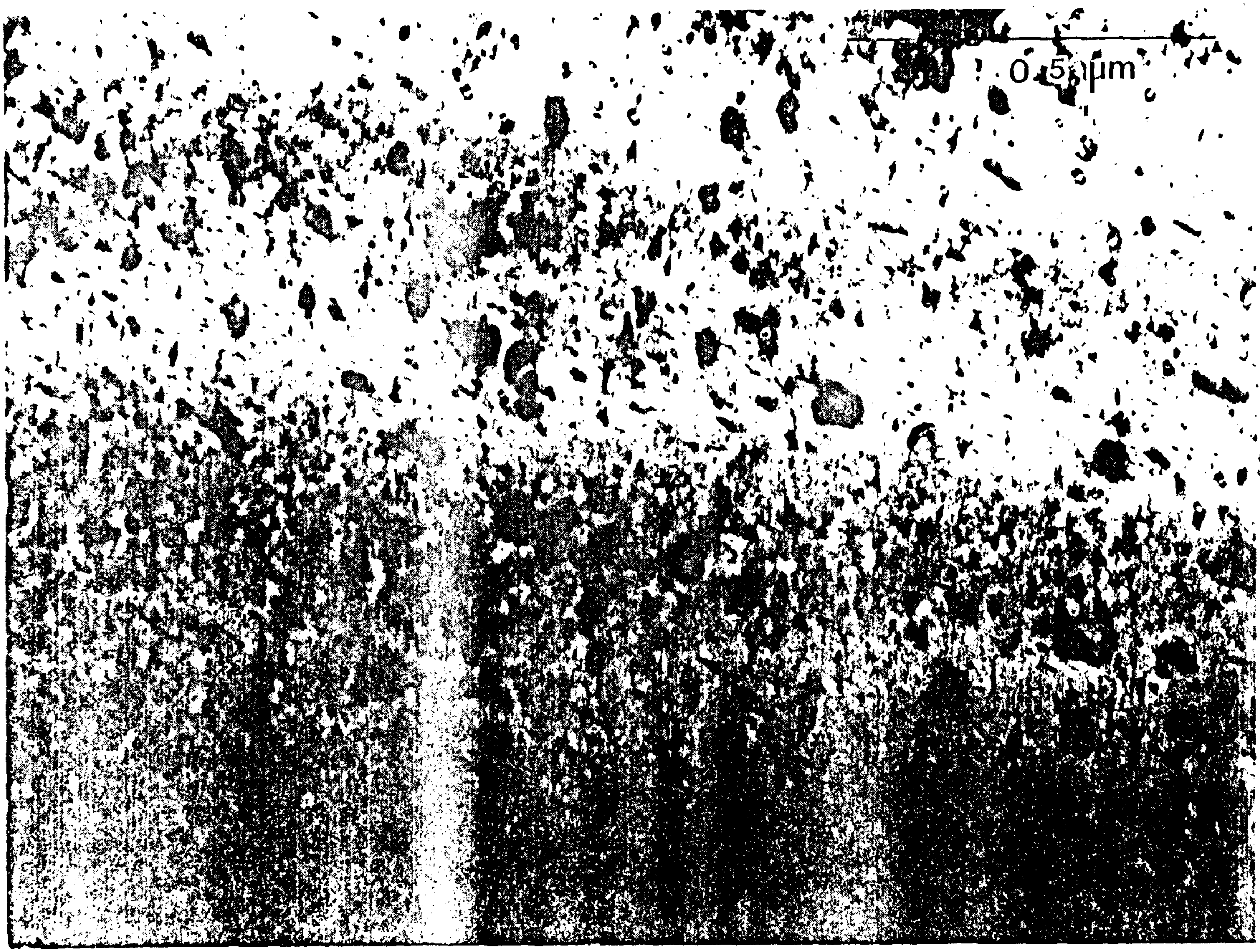


Fig. 11

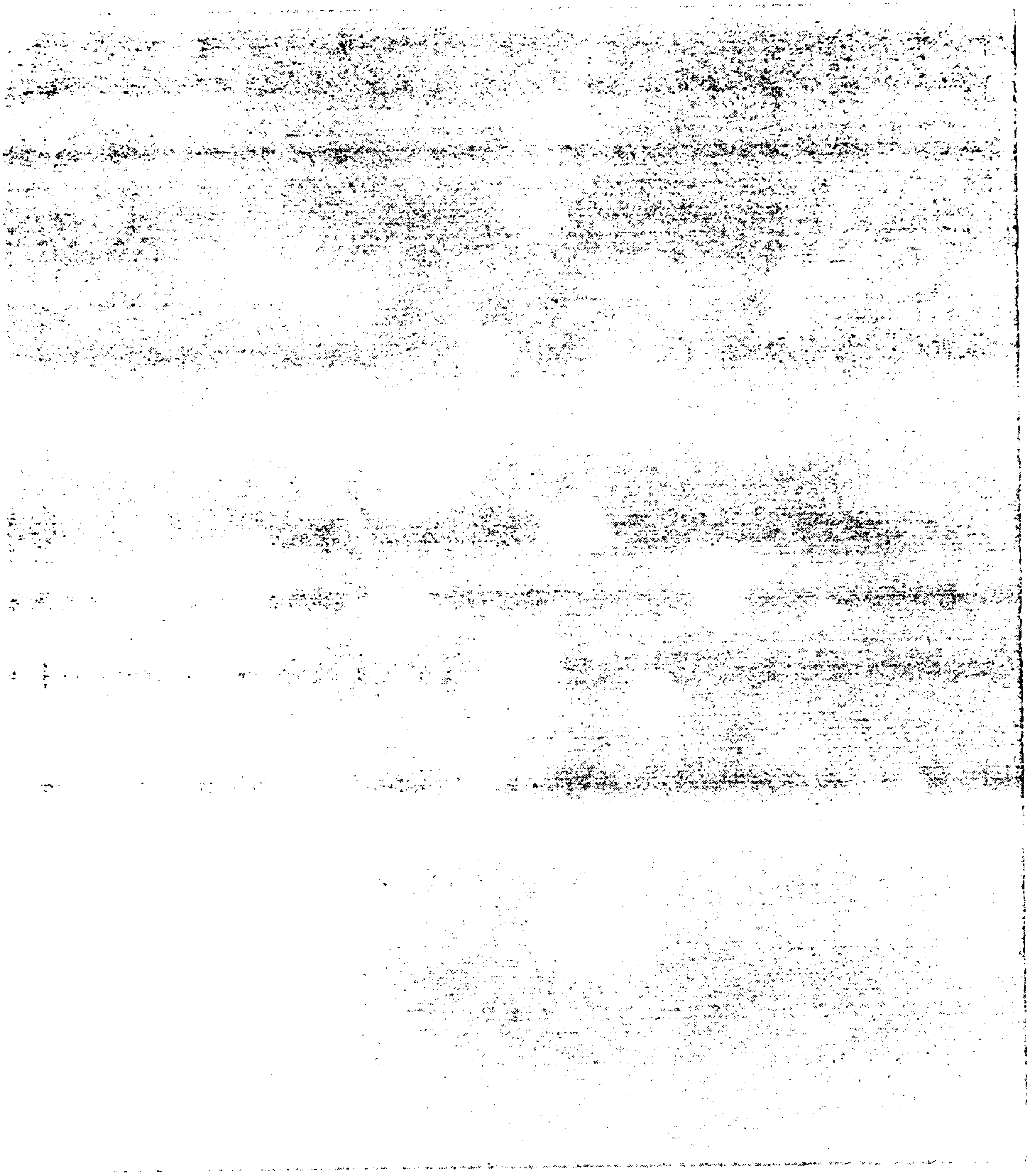


Fig. 12

END

DTIC

9- 86