CONF-8403148--2

MATERIALS SCIENCE WITH SYNCHROTRON RADIATION:
THE CASE FOR A SUPERPROBE*

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presentation to the

MAJOR MATERIALS FACILITIES COMMITTEE
NATIONAL RESEARCH COUNCIL

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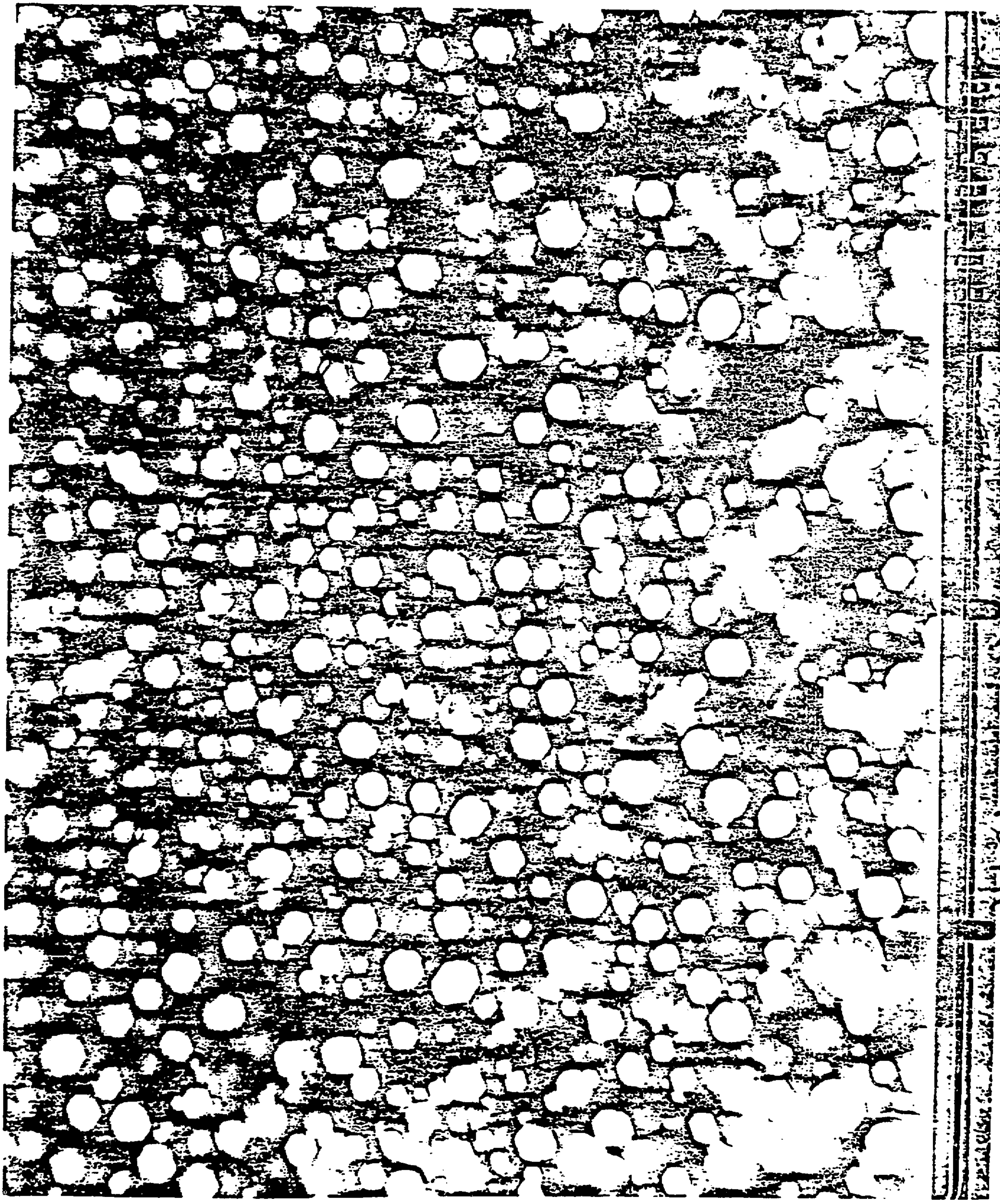
WE WILL TALK ABOUT THE FOLLOWING

I. THE MECHANICAL STRENGTH, DUCTILITY, DIFFUSION, CORROSION, AND ELECTRICAL PROPERTIES OF MATERIALS ARE PROFOUNDLY MODIFIED BY DEFECTS (BOTH STRUCTURAL AND IMPURITY) ABOUT WHICH WE NEED MICRO-CHARACTERIZATION.

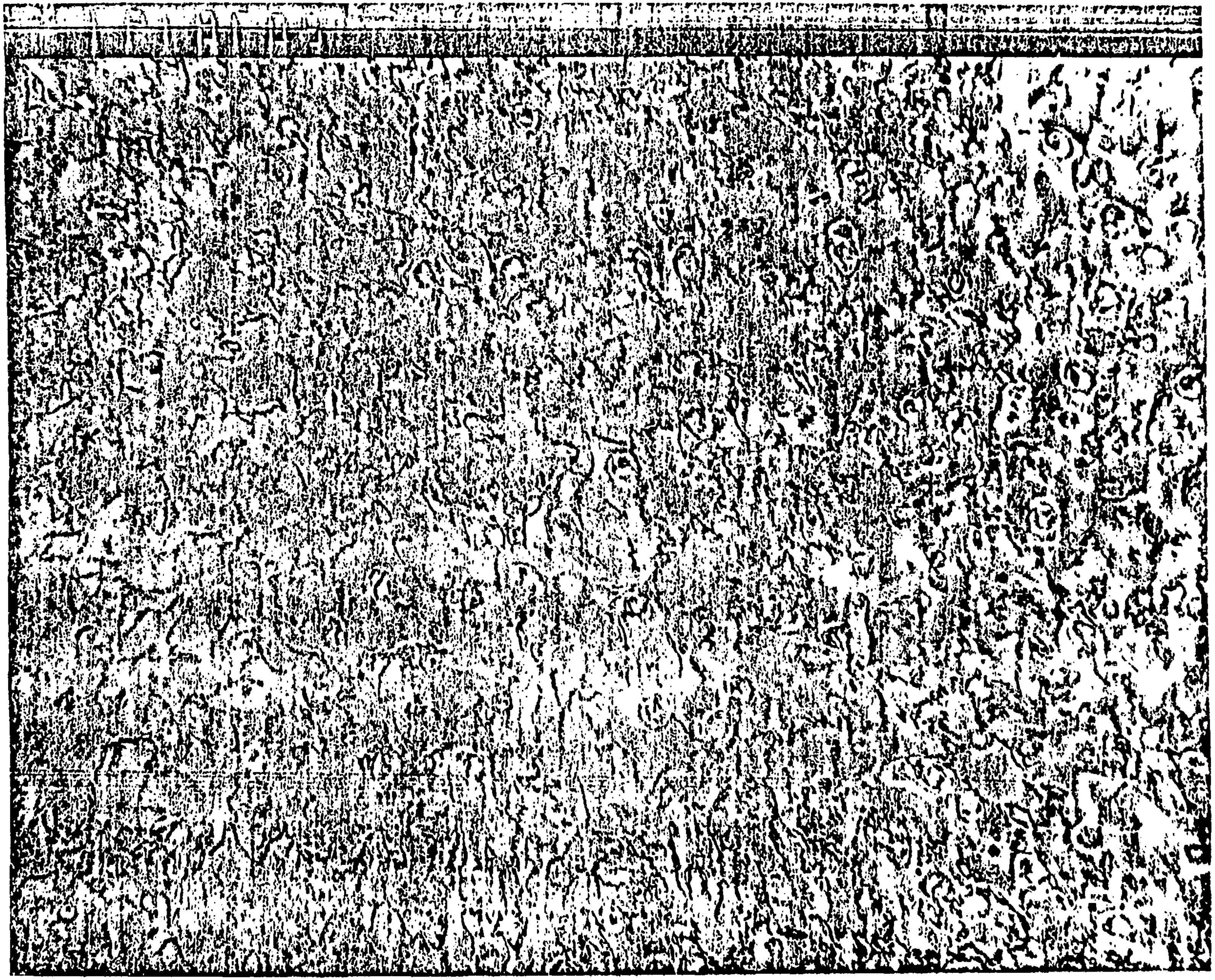
II. AN X-RAY MICROPROBE IS THE NEXT LEAP FORWARD IN MICRO-CHARACTERIZATION.

III. UNDULATORS ON A 6 GeV STORAGE RING WILL PROVIDE FOR AN X-RAY MICROPROBE OF EXTRAORDINARY SENSITIVITY.

20dpa at 675°C (no He injection)

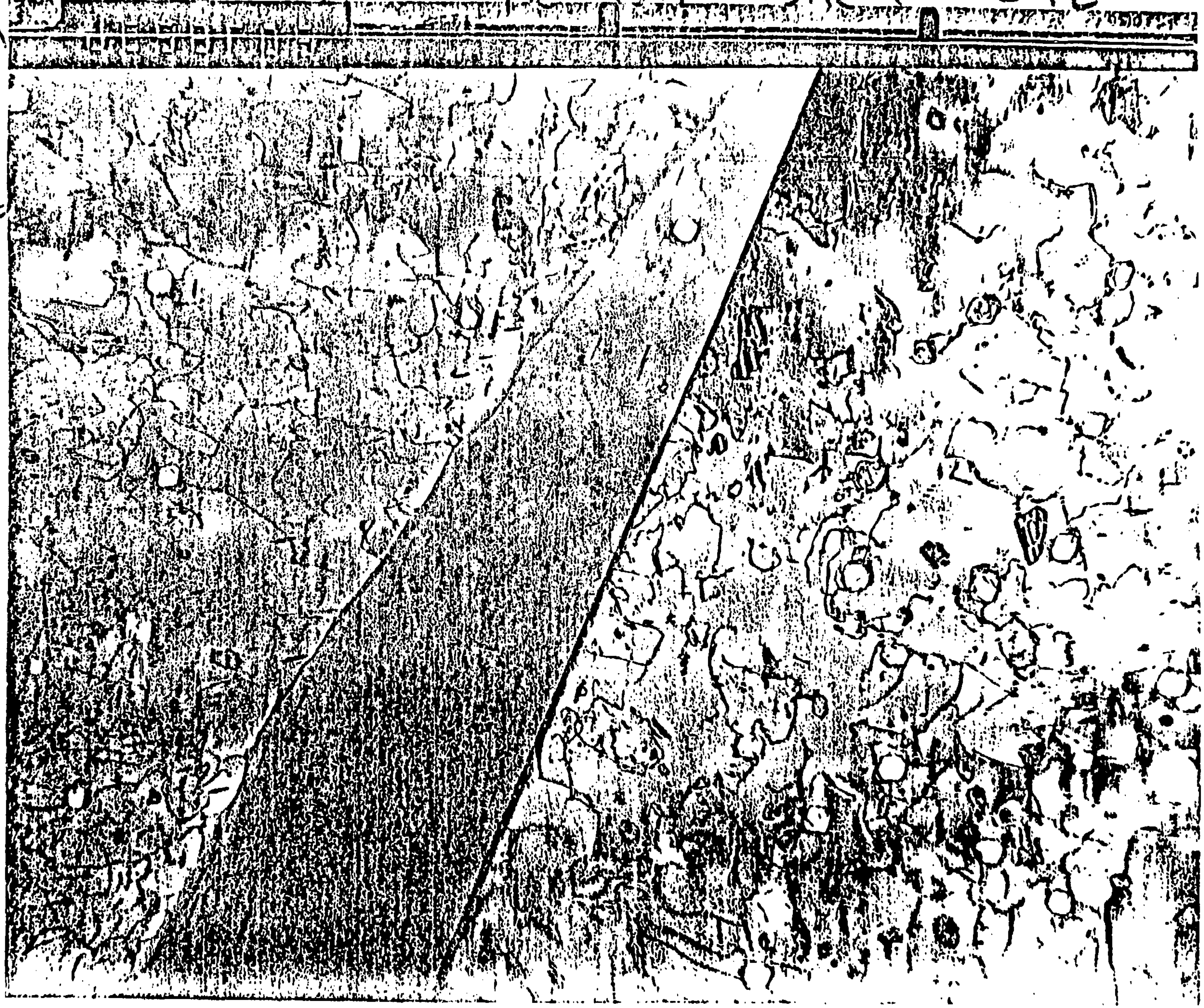


#78197 B3 70 Fe-13Cr-15Ni-0.8Si



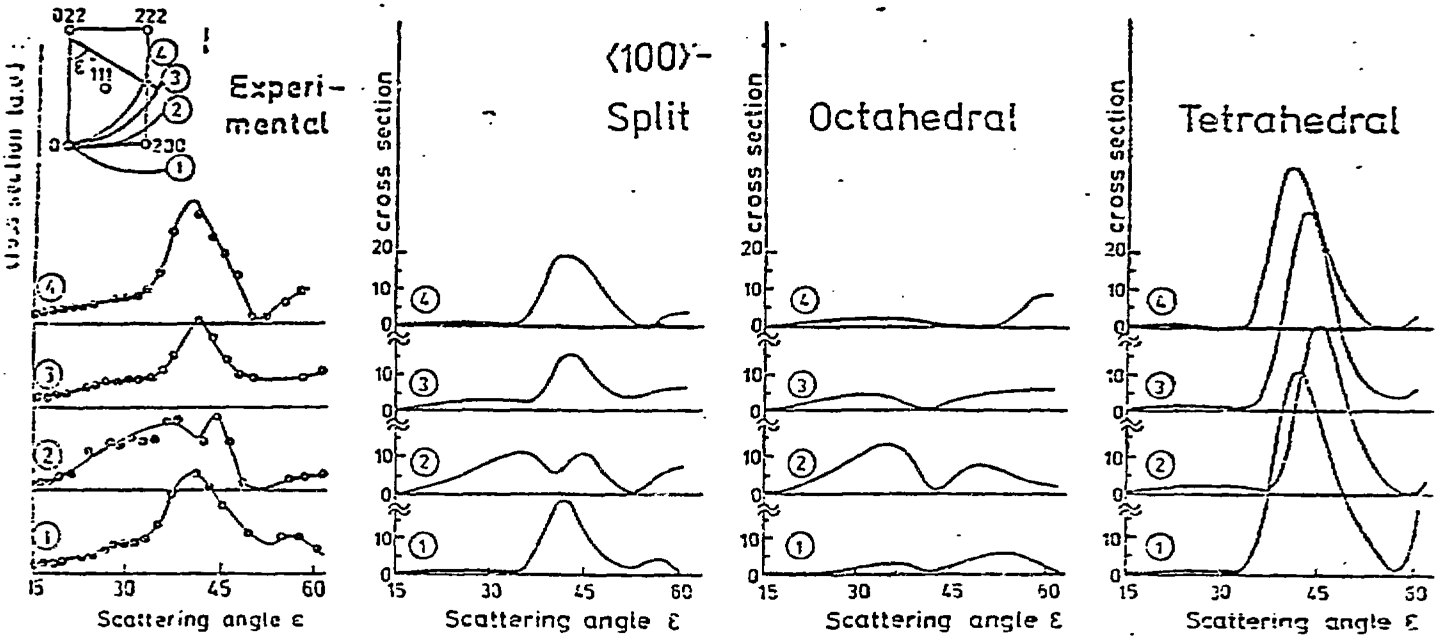
70 dpa at 675°C (no He injected)

H78236 B2 Fe-13Cr-15Ni + 0.2Ti



20 dpa at 675°C (no He-injection)

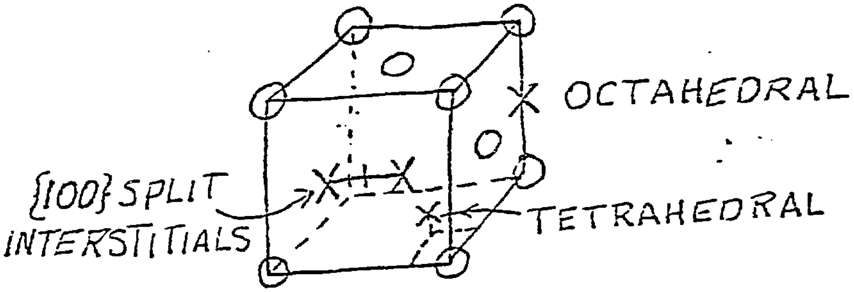
DIFFUSE X-RAY SCATTERING MEASUREMENTS SHOW INTERSTITIAL CONFIGURATION IN ELECTRON IRRADIATED ALUMINUM AT 4°K



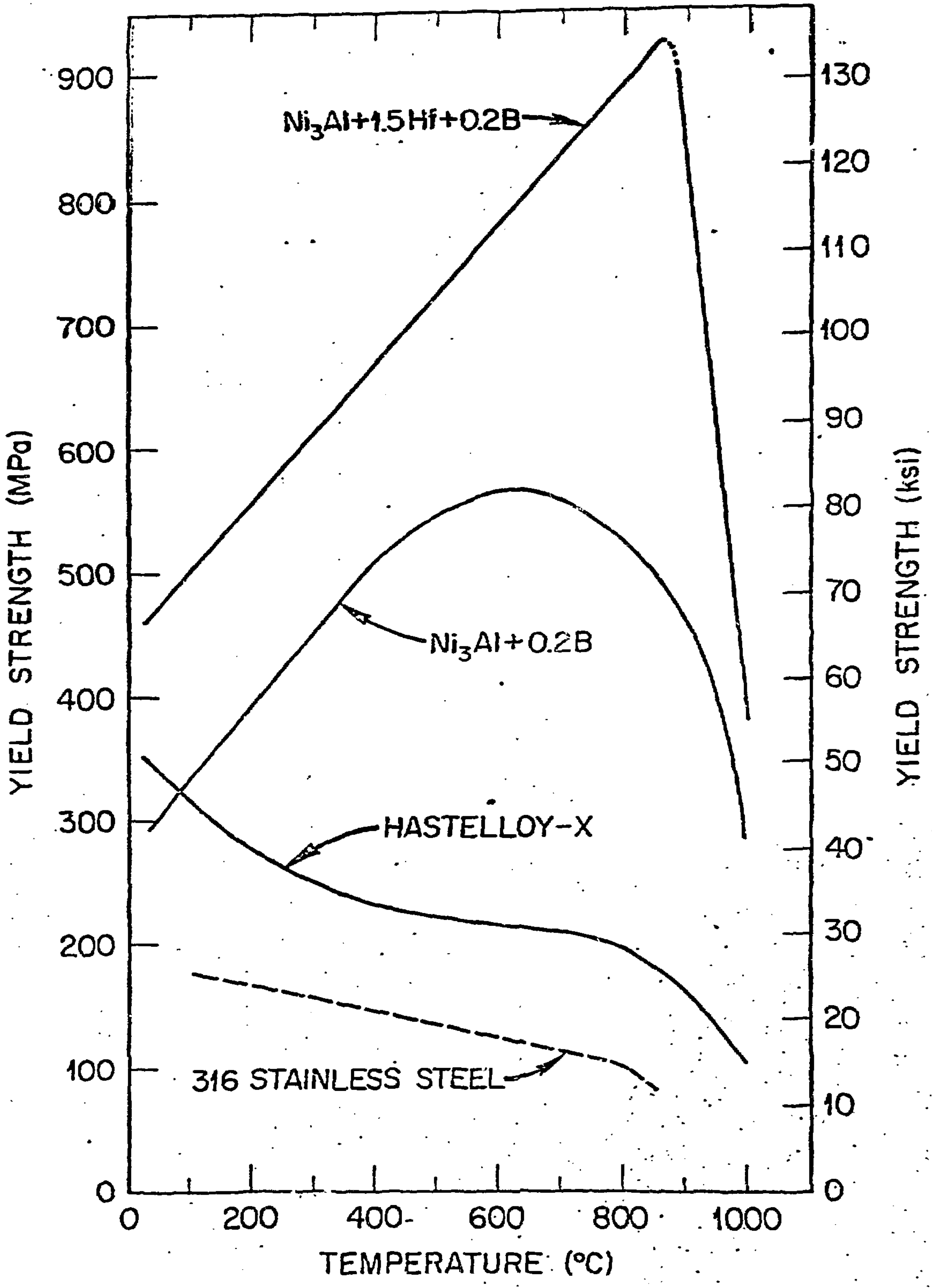
(P. Ehrhart, H. G. Haubold, and W. Schilling, Julich, Germany)

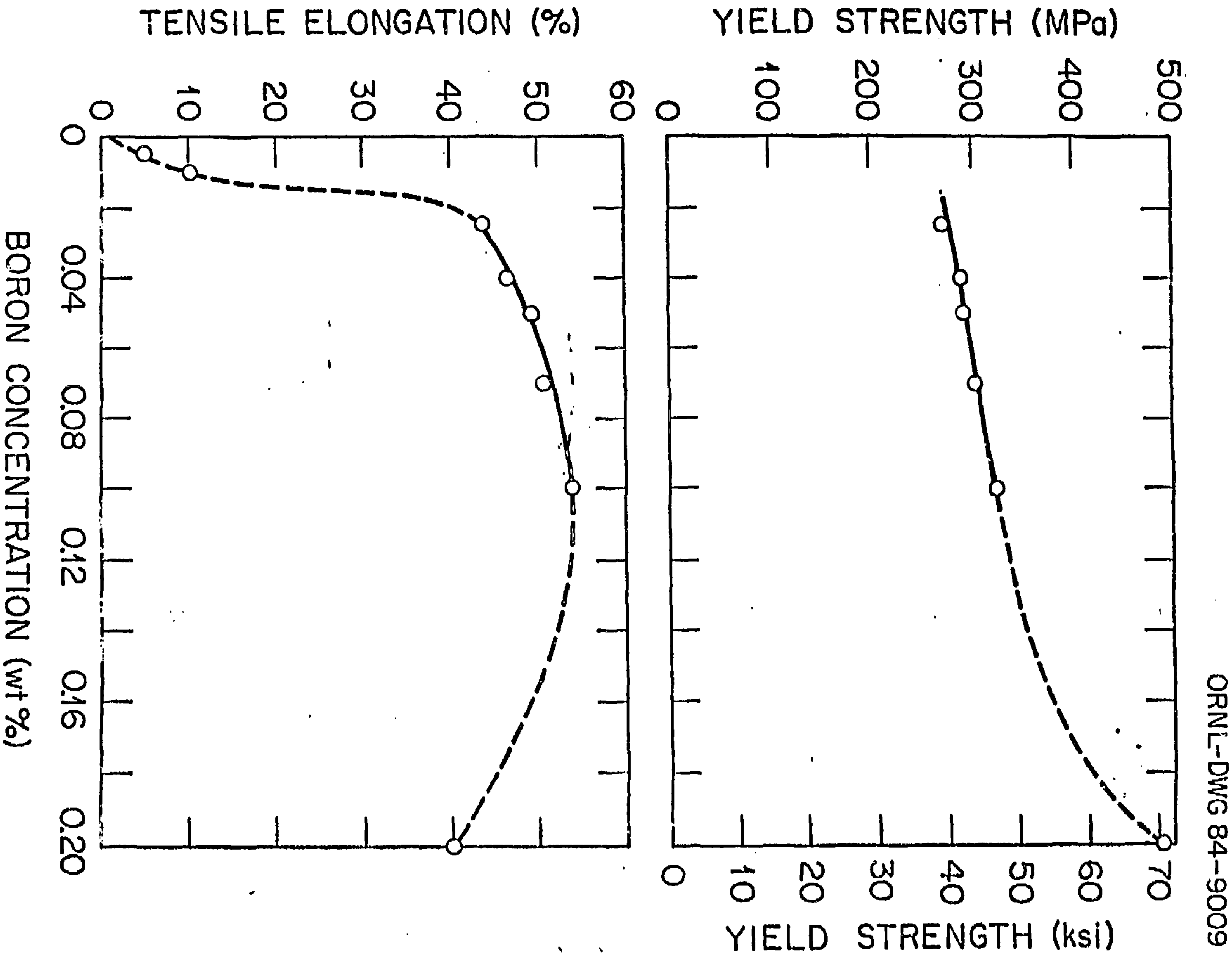
1 POINT DEFECT

10,000 ATOMS

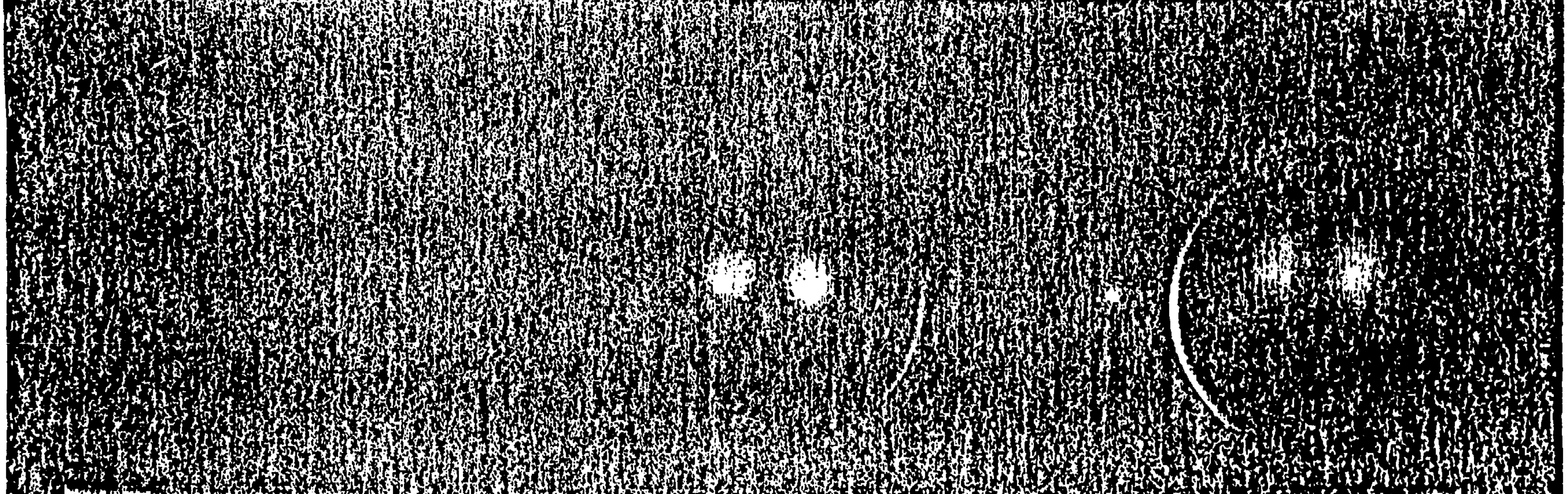


ORNL-DWG 83-15705



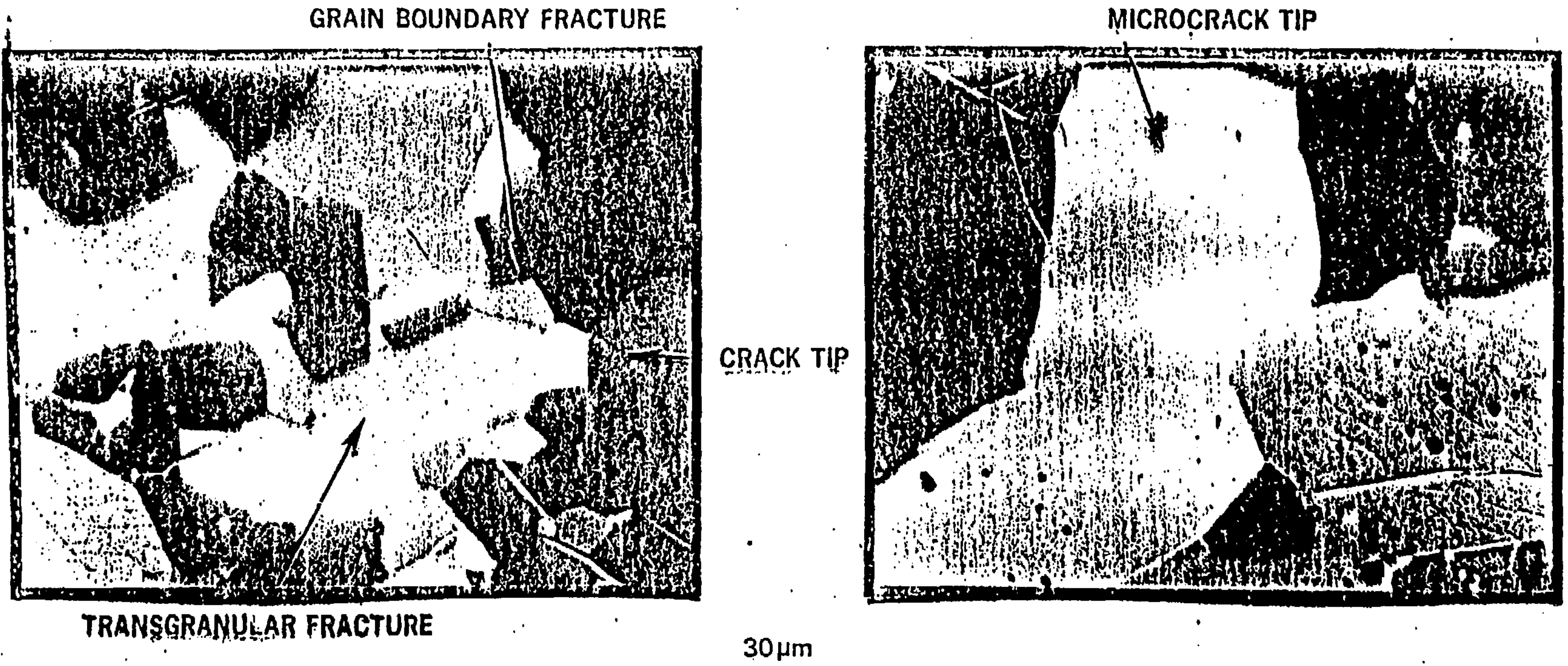

ORNL-DWG 84-9009
YIELD STRENGTH (MPa)
0
100
200
300
400
500
YIELD STRENGTH (ksi)
0
10
20
30
40
50
60
70
TENSILE ELONGATION (%)
0
10
20
30
40
50
60
BORON CONCENTRATION (wt %)
0
0.04
0.08
0.12
0.16
0.20

INTERMETALLIC ALLOYS BASED ON NICKEL ALUMINIDES CAN BE MADE MORE DUCTILE THAN STAINLESS STEELS



- THE ALUMINIDES ARE MUCH STRONGER THAN STAINLESS STEELS AND SUPERALLOYS AT ELEVATED TEMPERATURES

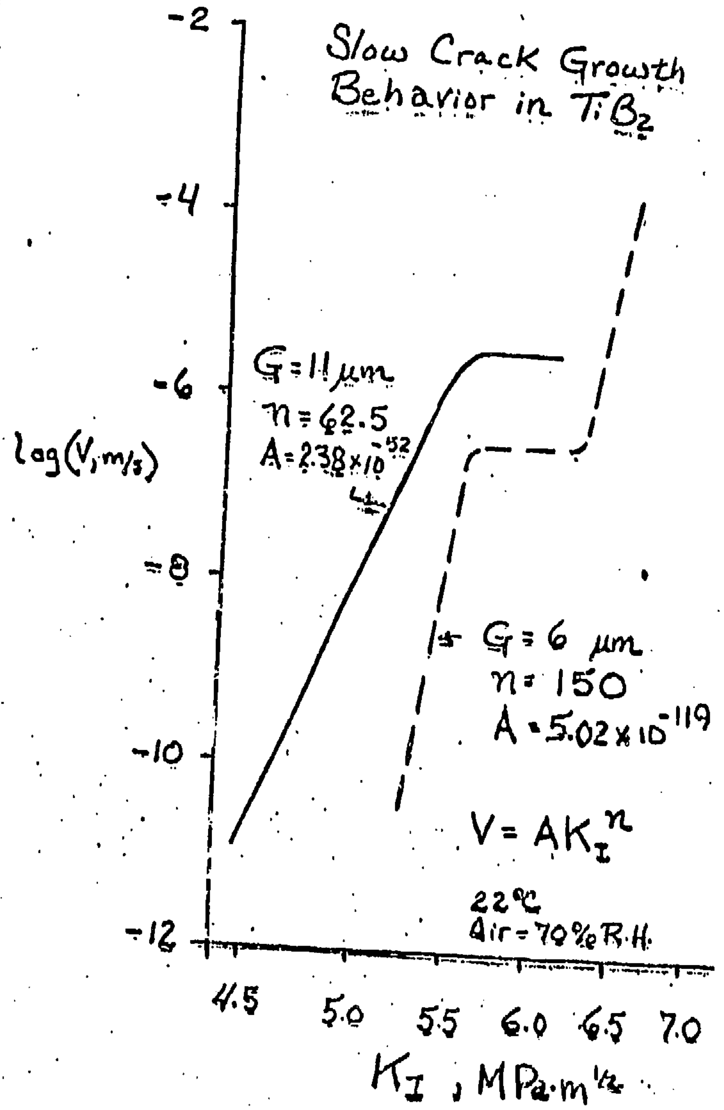
PURE TiB_2 CERAMIC EXHIBITS EXTENSIVE MICROCRACKING DUE TO THERMAL EXPANSION ANISOTROPY

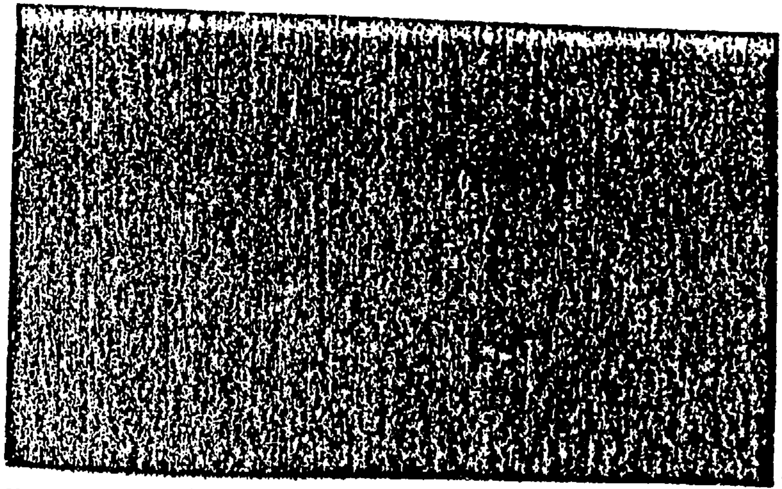


POLARIZED LIGHT

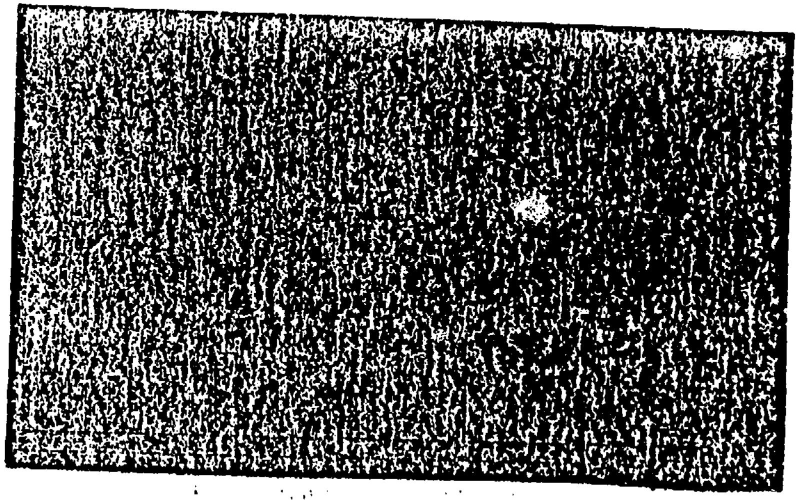
HOT PRESSING CONDITIONS

Temperature: 2050°C
Pressure: 25 MPa
Time: 4 h
Atm: Vac



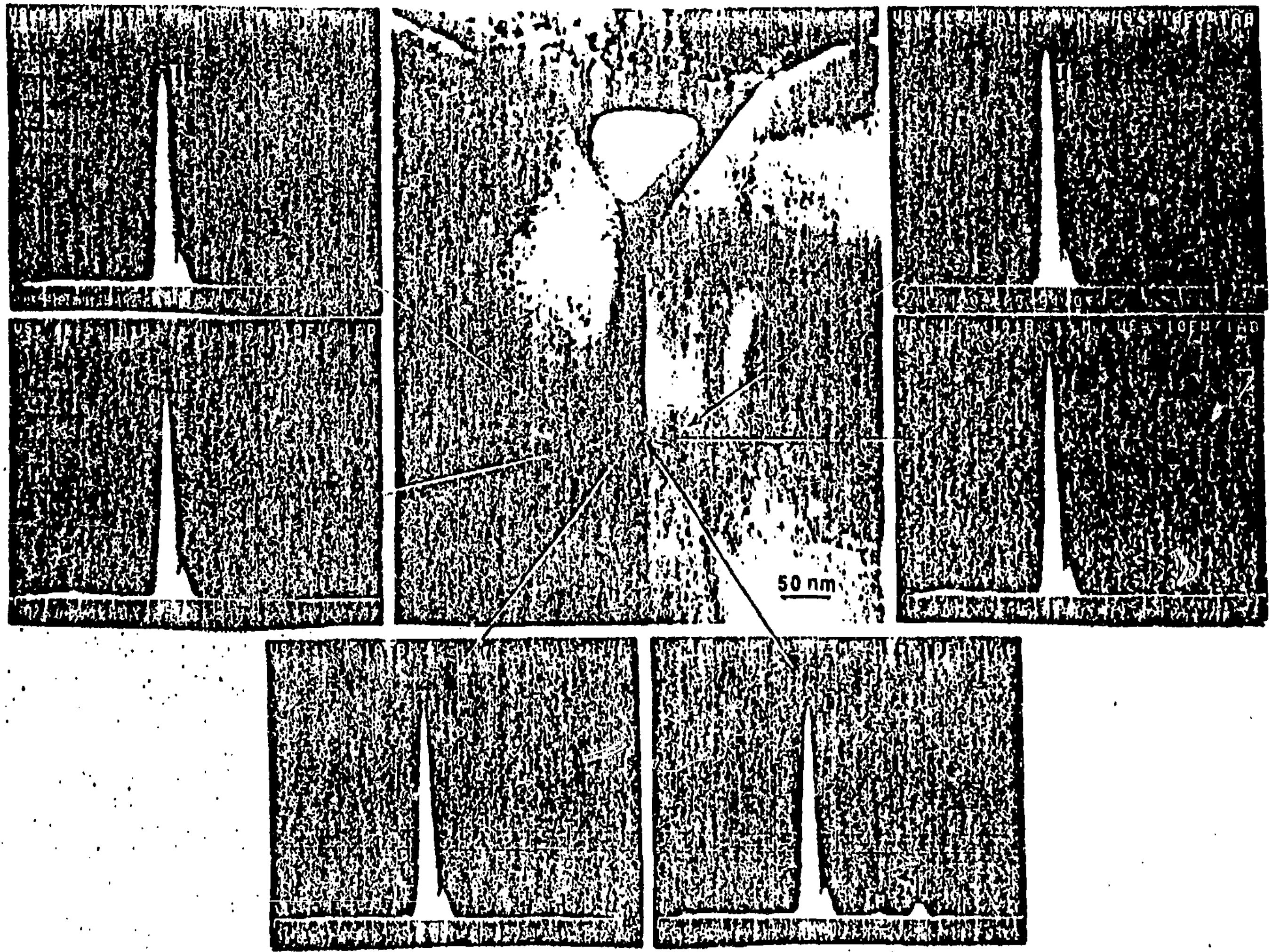


NT 90AD G_{ave} 11 μm σ_f = 450 MPa ×1000
Ni — 1.3 wt % E = 578 GPa
O_2 — 0.6 wt % ν = 0.115



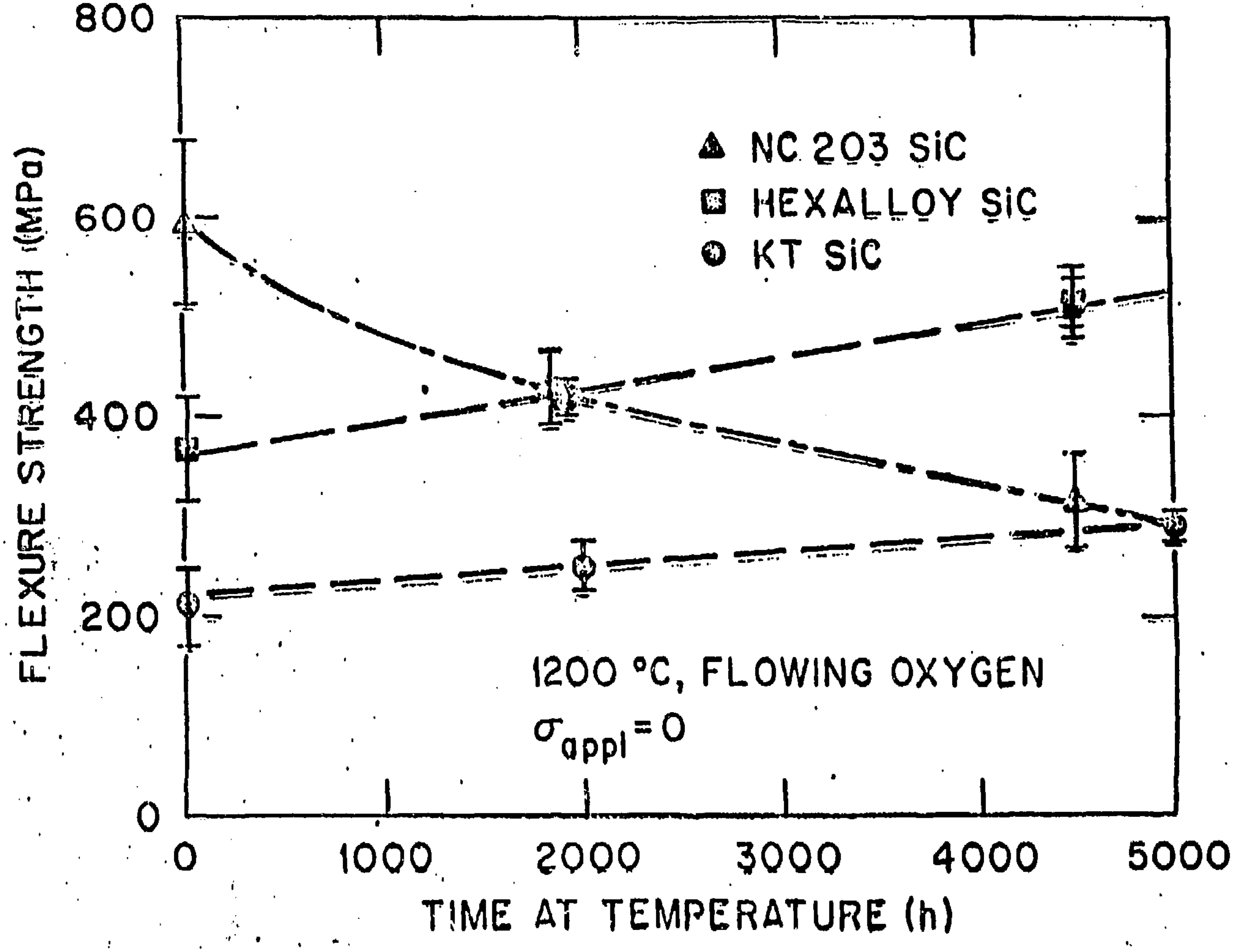
NT 90AB G_{ave} 6 μm σ_f = 720 MPa ×1000
Ni — 1.2 wt % E = 564 GPa
O_2 — 1.1 wt % ν = 0.115

X-RAY ENERGY DISPERSIVE SPECTROSCOPY (EDS) OF A NUMBER OF BOUNDARIES NEAR TRIPLE POINTS REVEALS THE PRESENCE OF Ni AND Fe



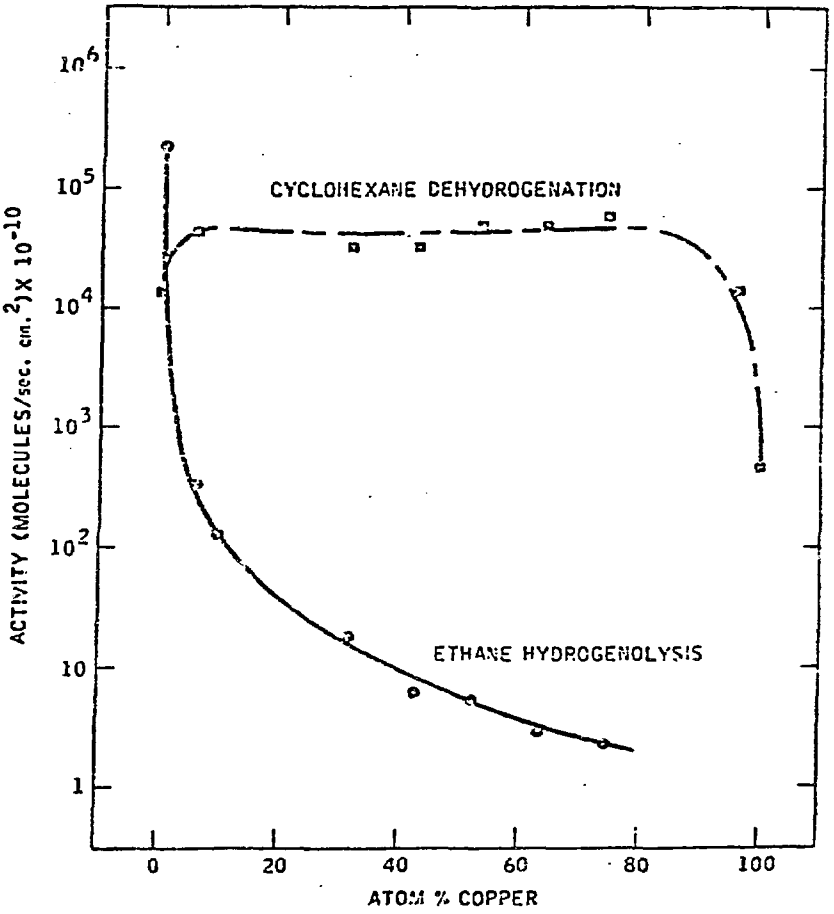
Quantitative analyses indicate that there is ∿ 8 at % Ni and ∿ 1.5 at % Fe in the analyzed regions at boundaries

STRENGTH RETAINED OF SiC AFTER OXIDATION AT 1200°C IN FLOWING OXYGEN DEPENDS UPON INITIAL COMPOSITION

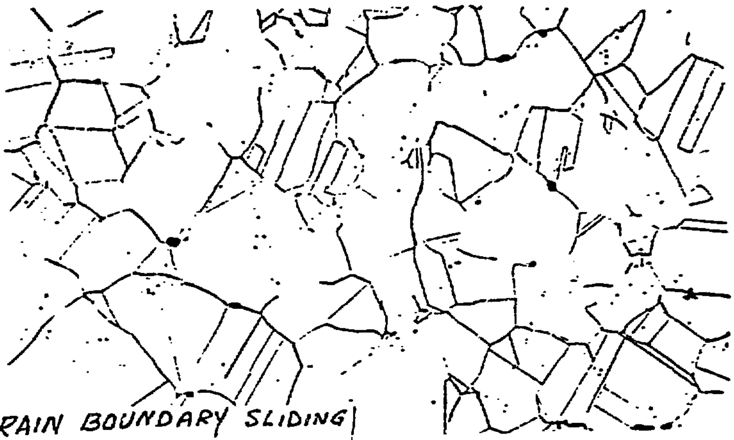


"COMPLEXITY OF CATALYTIC PHENOMENA AND OUR LIMITATIONS IN OBTAINING STRUCTURAL AND ELECTRONIC INFORMATION AT A SUFFICIENTLY MICROSCOPIC LEVEL HAVE IMPEDED OUR SCIENTIFIC UNDERSTANDING."

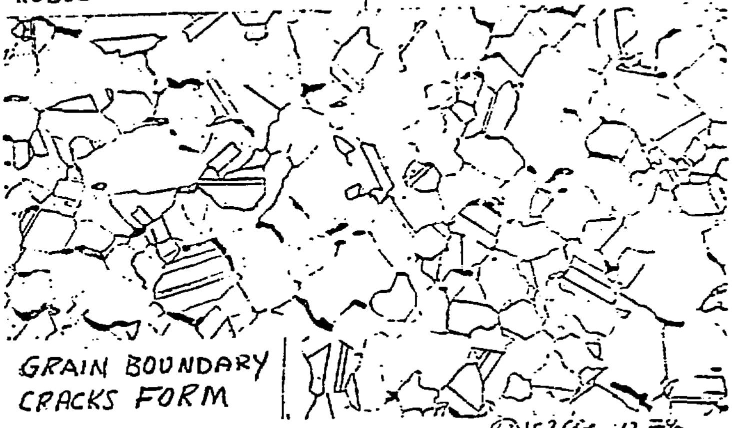
John H. Sinfelt: Structure of metal catalysts



CREEP RUPTURE OF Ni+20% Cr



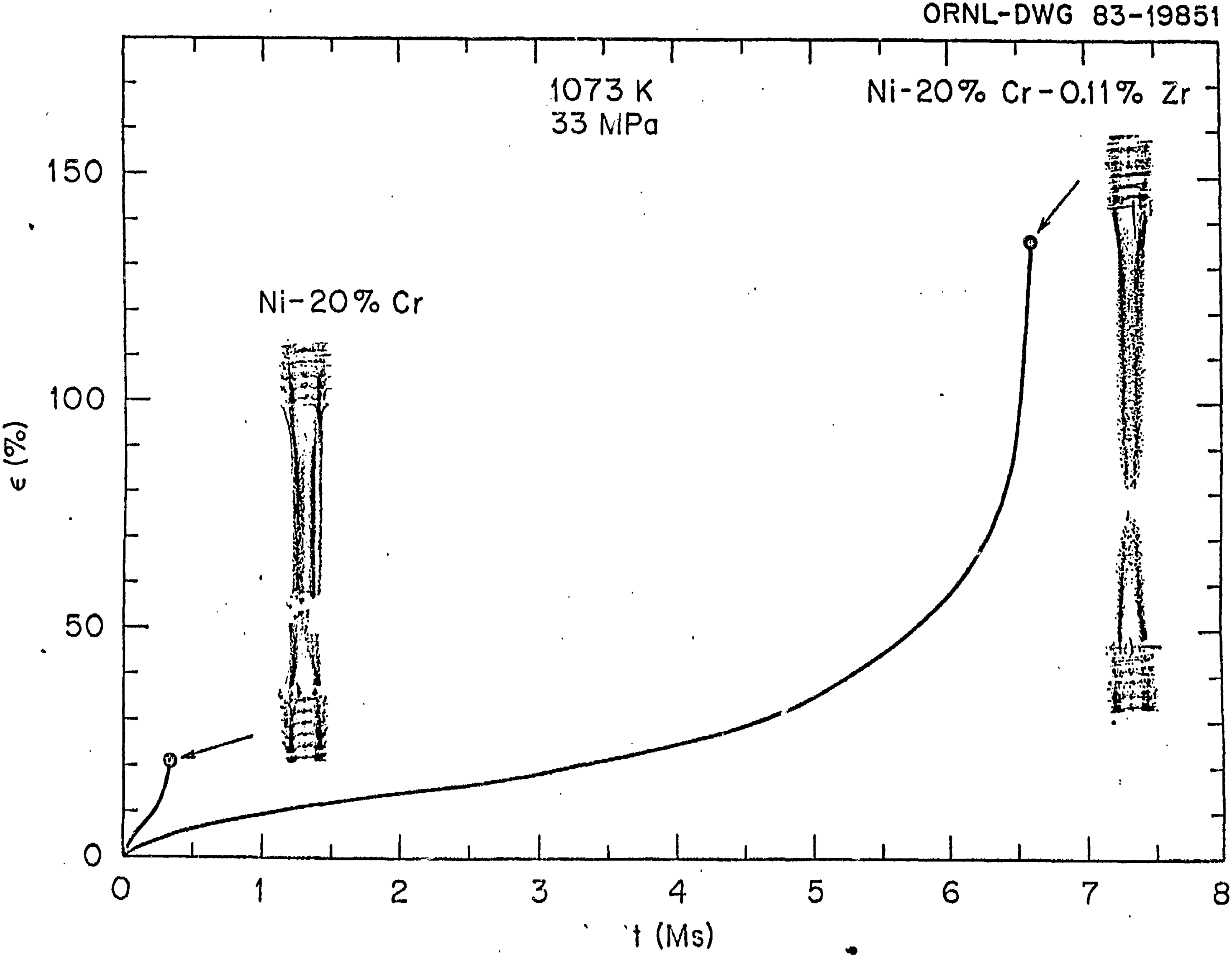
GRAIN BOUNDARY SLIDING PRODUCES VOIDS

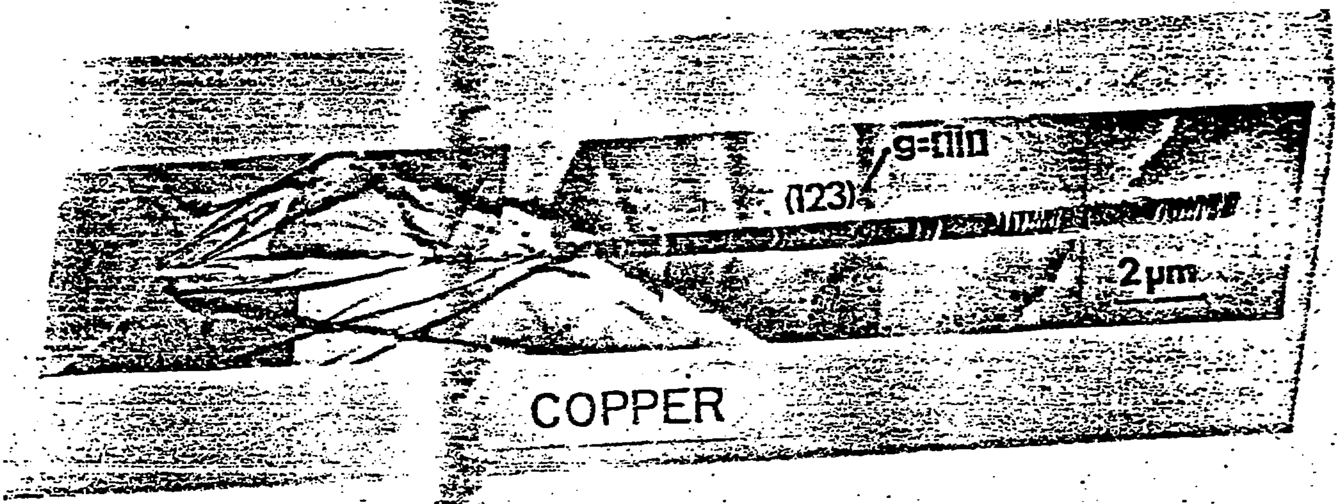


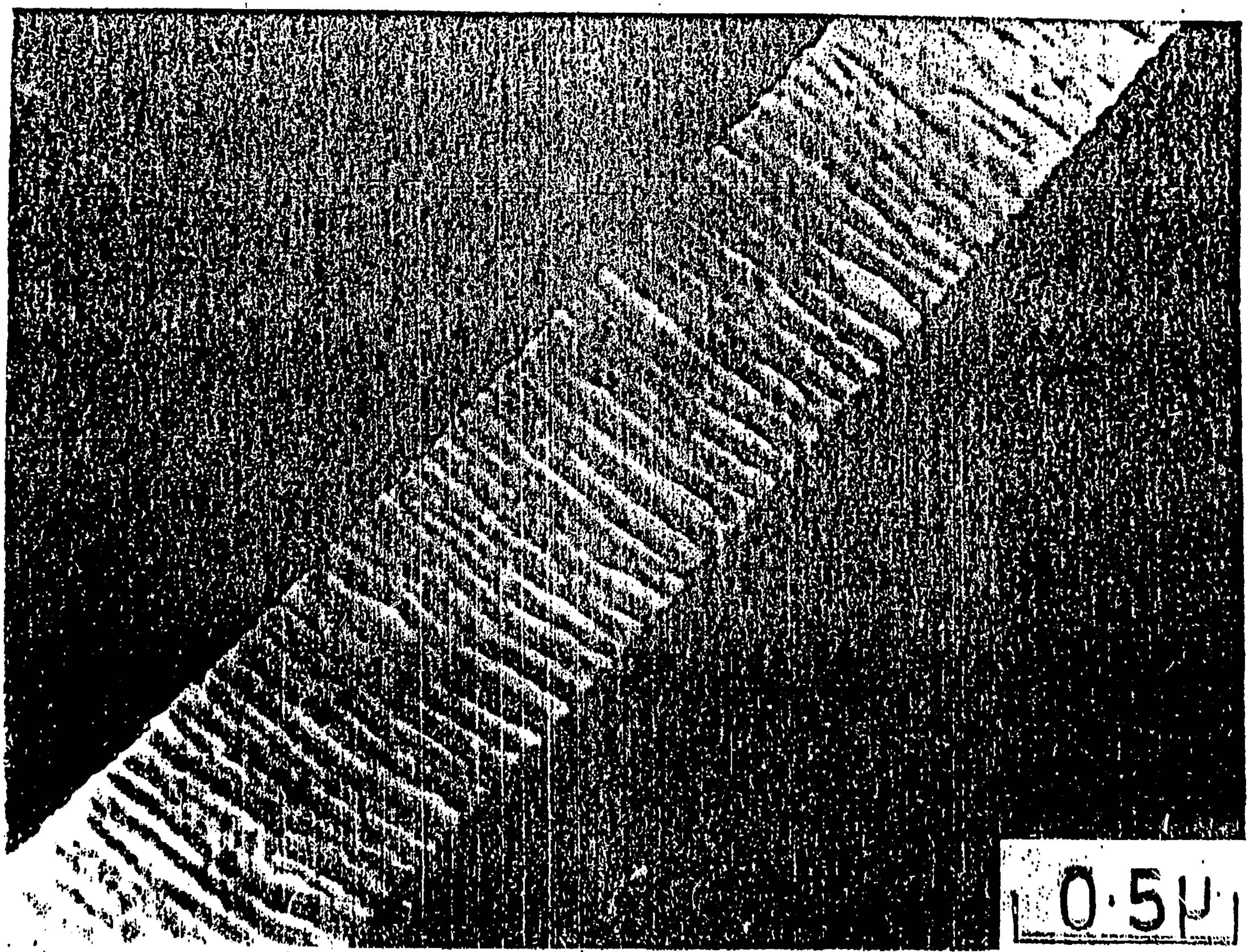
GRAIN BOUNDARY CRACKS FORM

㊷ Ni20Cr, 12.7%
34 MPa, 163 KS

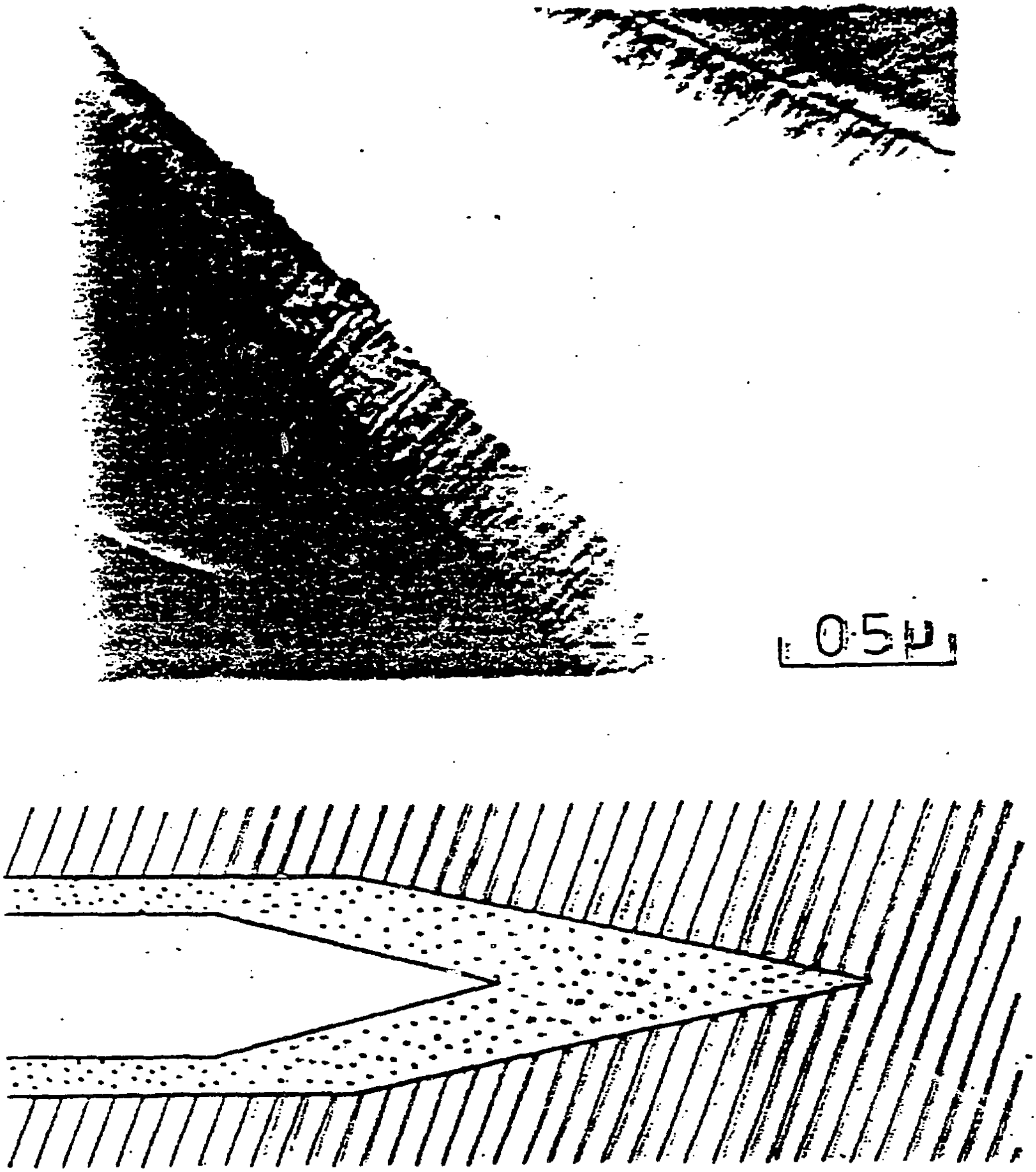
SPECIMEN RUPTURES BY GRAIN BOUNDARY FAILURE


ORNL-DWG 83-19851
1073 K
33 MPa
Ni-20% Cr
Ni-20% Cr-0.11% Zr
ϵ (%)
0
50
100
150
t (Ms)
0
1
2
3
4
5
6
7
8


$g=[1\bar{1}0]$
(123)
2 μm
COPPER

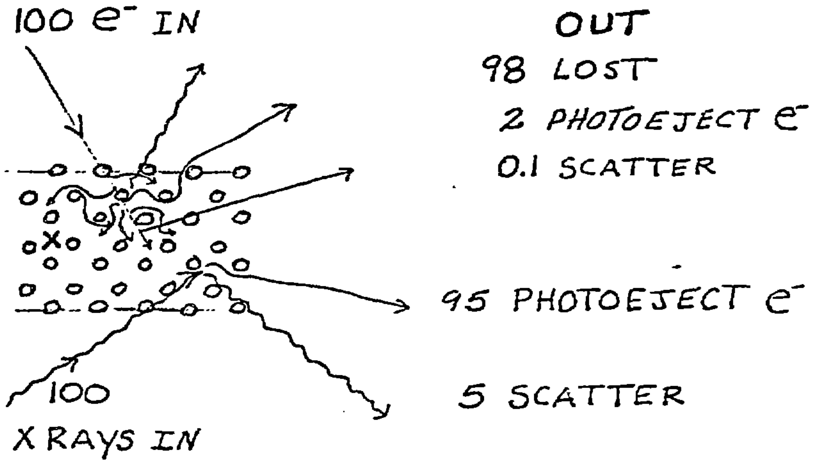


Transmission electron micrograph of a craze.



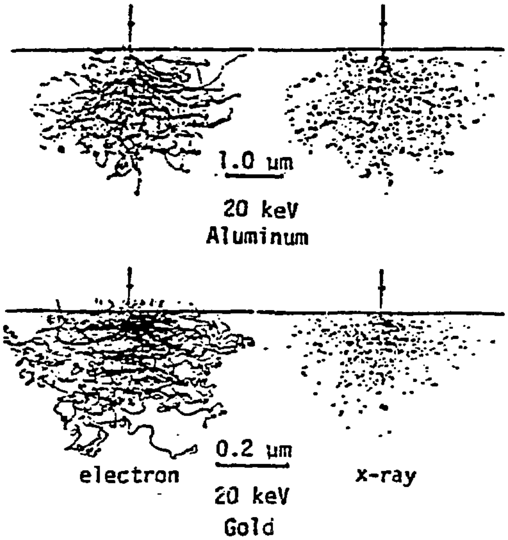
Variation of the microstructure along the length of a craze.
(a) transmission electron-micrograph of a fractured craze;
(b) proposed model for craze.

X RAYS ARE MOST DESIRED PROBE FOR MATERIALS



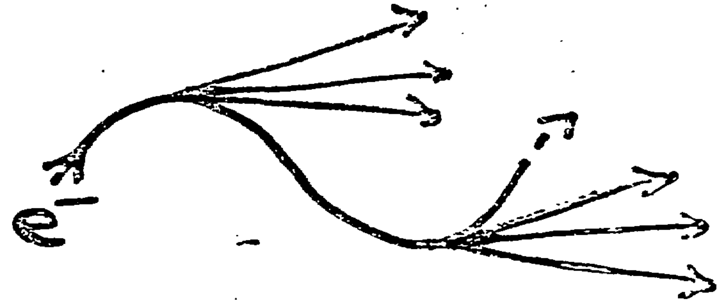
ORNL

INTERACTION VOLUME OF 20 keV ELECTRONS RANGES FROM 2 μm IN ALUMINUM TO 0.4 μm IN GOLD FOR THICK SAMPLES

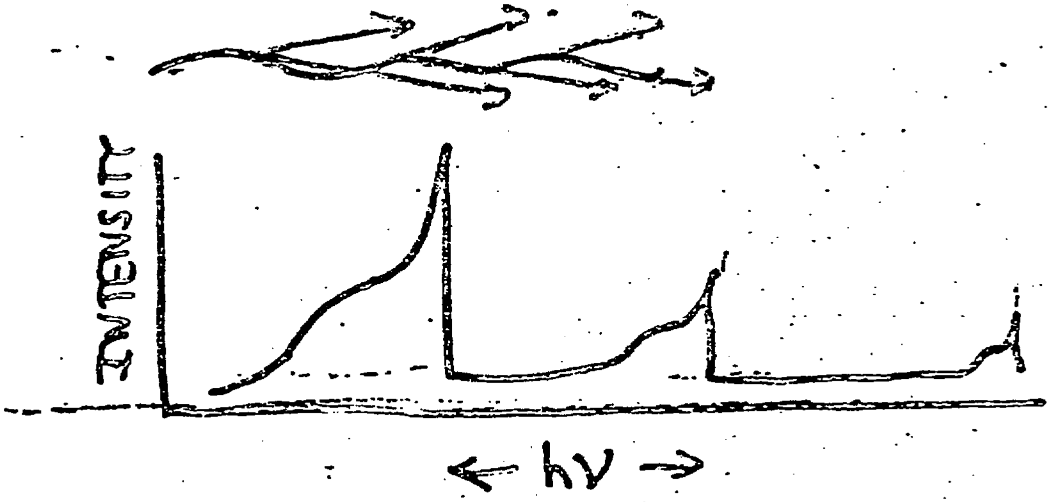


From Curgenver and Duncumb
TIRL Report 303, Essex, England, 1971

WIGGLERS SUPERIMPOSE THE RADIATION FROM SEVERAL ARCS.

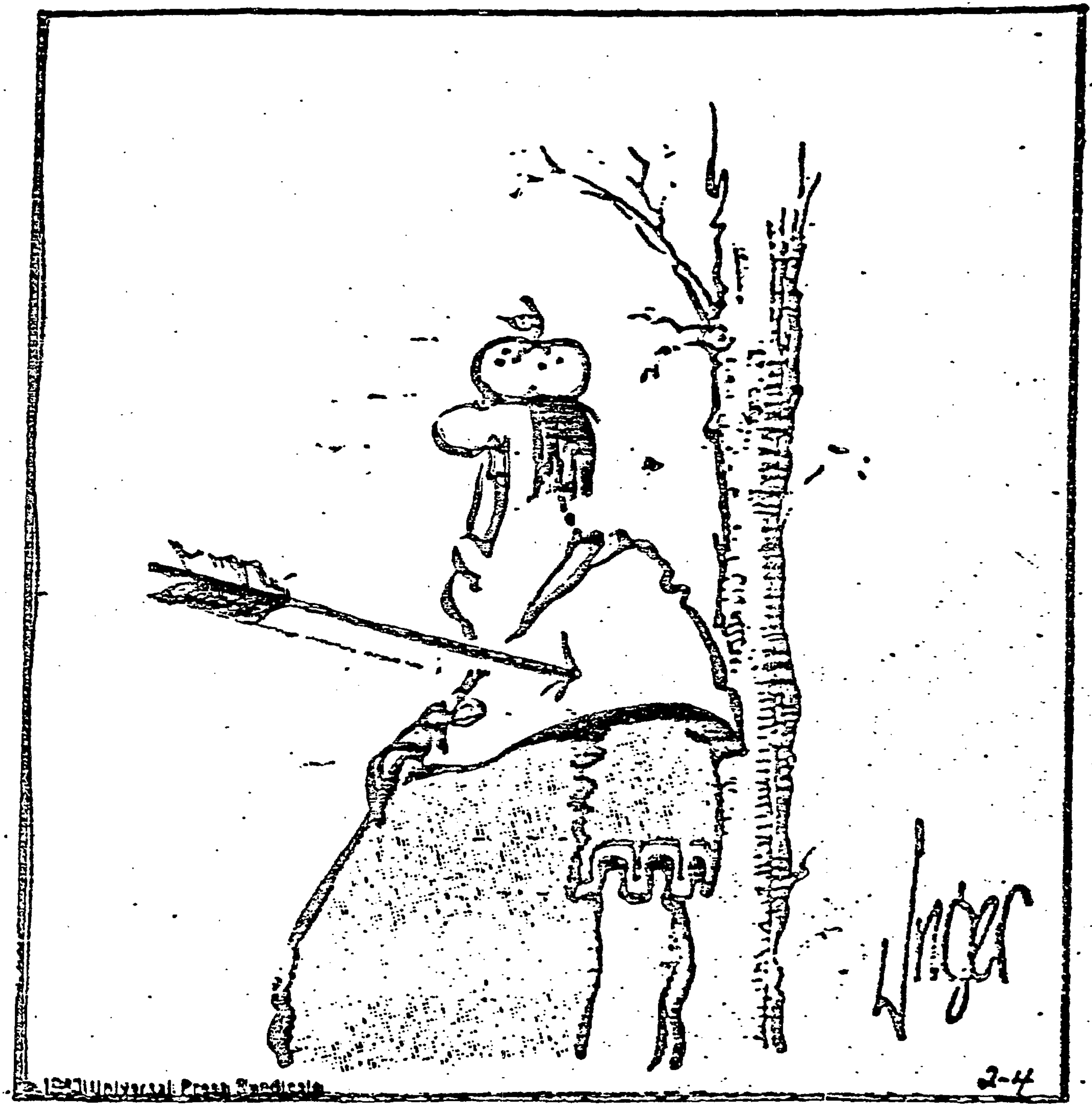


UNDULATORS PROVIDE VERY BRIGHT QUASI-MONOCHROMATIC RAD.



—SOMETIMES UNUSABLE FLUX IS WORSE THAN NO FLUX—

HERMAN



"Up and left."

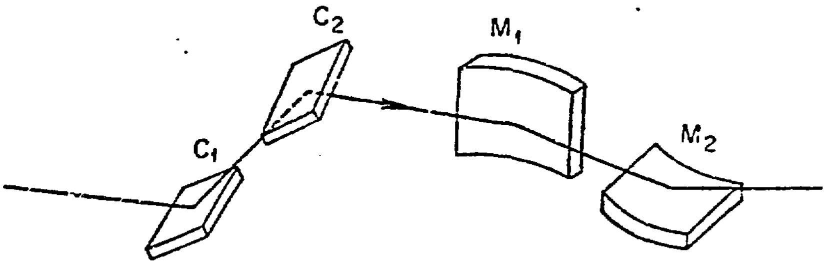
DEMAGNIFY THE SOURCE SIZE WHILE MAINTAINING THE FLUX

- SOURCE SIZE $2\sigma_X = 0.8\ \mu\text{m}$, $2\sigma_Y = 0.2\ \mu\text{m}$
- UNDULATOR DIVERGENCE $2\sigma_{X'} = 0.01$ MRAD, $2\sigma_{Y'} = 0.01$ MRAD

I. FRESNEL ZONE PLATES: TOO TRANSPARENT FOR HARD X RAYS, CHOICE BELOW 1 KEV

			ACCEPTANCE AT 12 KEV		
		DEMAGNIFICATION	CYLINDRICAL MRAD	ELLIPTICAL MRAD	PROBE SIZE µM • µM
II.	MIRRORS	100:1	0.013	0.034	8 × 2
		1000:1	0.0013	0.0034	0.8 × 0.2
III.	MULTILAYERS	100:1	0.026	0.136	8 × 2
		1000:1	0.0026	0.0136	0.8 × 0.2
IV.	CRYSTALS	100:1	0.058	0.68	8 × 2
		1000:1	0.0058	0.068	0.8 × 0.2

V. OPTICS



NONDISPERSIVE MULTILAYERS OR CRYSTALS FOLLOWED BY CROSSED ELLIPTICAL OR CYLINDRICAL MIRRORS

GAIN IN X-RAY MICROPROBE PERFORMANCE WITH 6 GeV RING

	14 keV X-rays 2.5 GeV, 500 mA Wiggler	14 keV X-rays 6 GeV, 200 mA Undulator	100 keV e^- Electron microprobe field emission
BRIGHTNESS P or $e^-/s\ \mu m^2$ mrad	10^{16}	2×10^{19}	3×10^{19}
INTENSITY P or e^-/Area s	$\frac{5 \times 10^{12}}{10\ \mu m^2\ 280\ eV\ s}$	$\frac{2 \times 10^{15}}{10\ \mu m^2\ 10\ eV\ s}$	
	$\frac{5 \times 10^{11}}{\mu m^2\ 280\ eV\ s}$	$\frac{1 \times 10^{14}}{\mu m^2\ 10\ eV\ s}$	$\frac{6 \times 10^{13}}{\mu m^2\ s}$
	$\frac{1 \times 10^{9}}{500\ Å^2\ 280\ eV\ s}$	$\frac{3 \times 10^{11}}{500\ Å^2\ 10\ eV\ s}$	
			$\frac{6 \times 10^{9}}{30\ Å^2\ s}$
			$\frac{10^{7}}{4\ Å^2\ s}$

200 probes, MDL = 50 ppm/100 sec
1100 SEM, MDL = 500 ppm/100 sec
4000 SEM, microscopy only

AN X-RAY PROBE CAN ACHIEVE SMALL DETECTABLE LIMITS

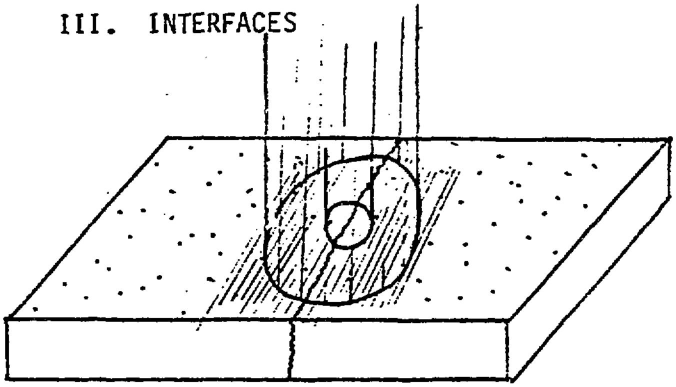
I. $$\text{MINIMUM DETECTABLE LIMIT} = \frac{3.29\ (\text{Mass Fraction})(\text{Background Counts})^{1/2}}{\text{Signal Counts}}$$

II. $$\frac{\text{Signal Counts}}{\text{Sec ppm}} = (\text{Thick-Target Yield})\left(\frac{\text{Incident Photons}}{\text{Sec}\quad \mu m^2}\right)$$

$$\times\ (\text{Solid Angle} = 10^{-3}) \times 10^{-6}\ \text{Mass Fraction}$$

$$\frac{N_s}{\text{Sec ppm}} = 0.1 \times \frac{10^{14}}{\text{Sec } 1\ \mu m^2} \times 10^{-9} = 10^{4}\ \frac{\text{Counts}}{\text{Sec ppm}}\ \text{in } 1\ \mu m^2\ \text{Spot}$$

III. INTERFACES



$$1\ \text{Atom Plane} = 2\ \text{Å}$$

$$\frac{1\ \mu m}{2\ \text{Å}} = 5000\ \text{Atomic Planes}$$

$$\frac{1\ \text{Monolayer}}{5000\ \text{Planes}} = 200\ \text{Parts Per Million}$$

WITH ALL THE IMPURITY IN THE INTERFACE

$$\text{MDL} = 3.29 \times 1\ \text{ppm} \times \left(\frac{1}{10}\right)^{1/2} \times \frac{1}{(10{,}000)^{1/2}} = 10.5\ \text{ppb/sec}$$

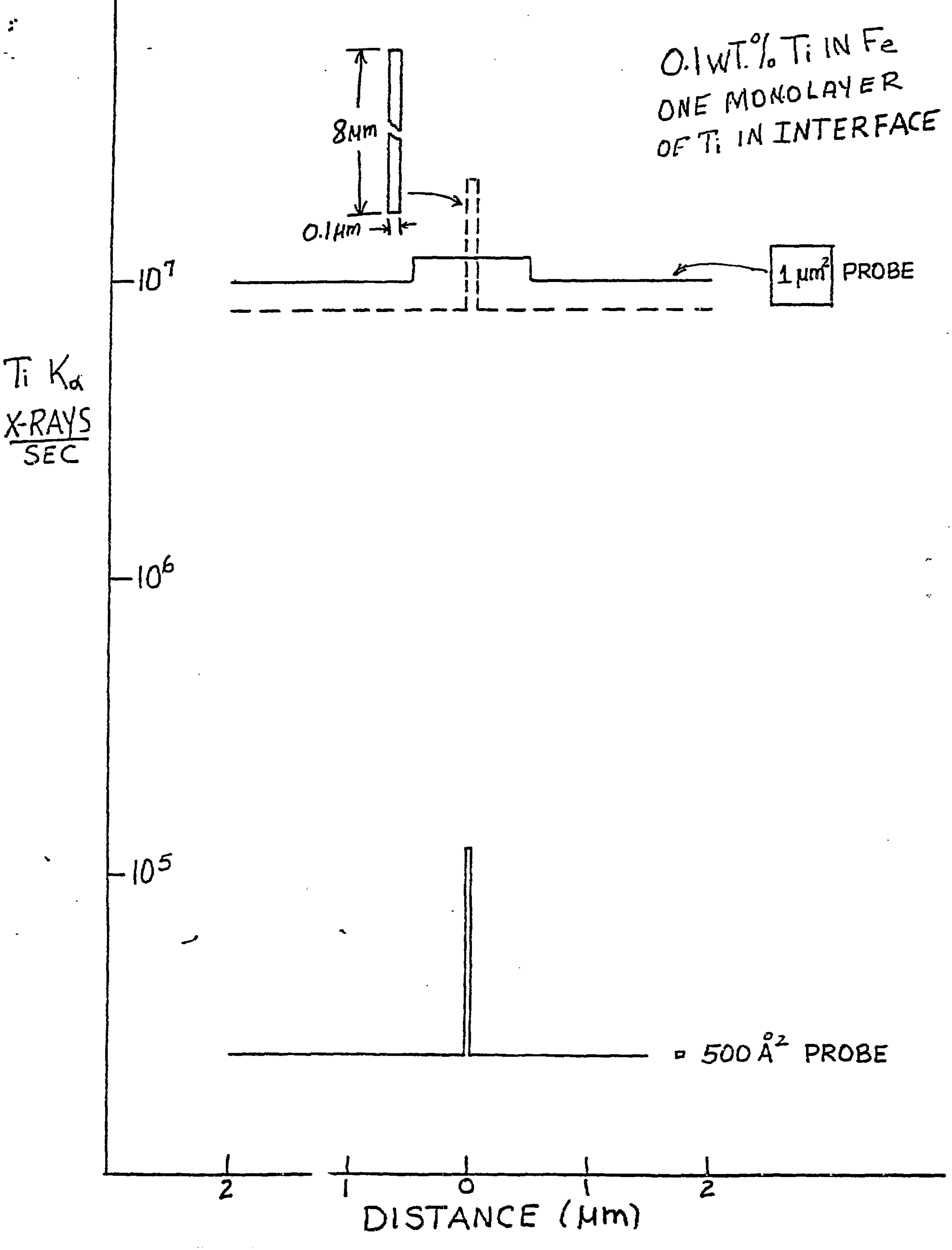
or

$$\text{MDL} = 5 \times 10^{-5}\ \text{of a monolayer/sec}$$

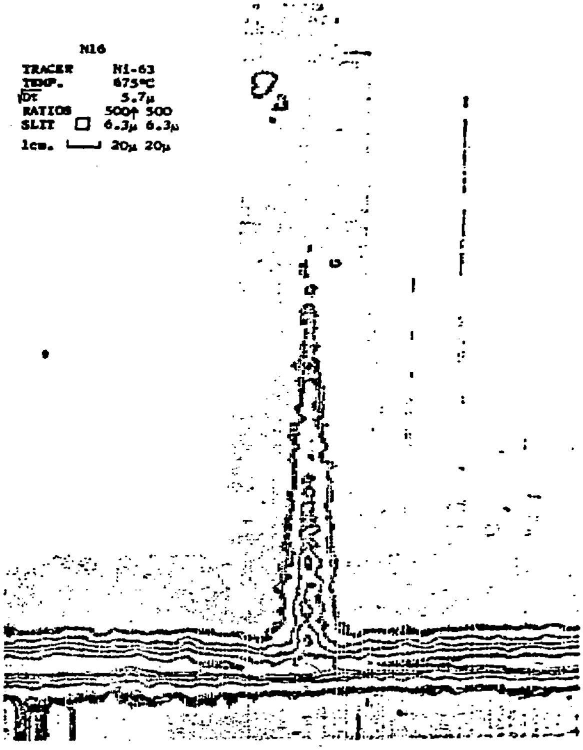
IV. IN DIRTY ALLOYS AND CERAMICS WITH 0.1 wt % IMPURITY

A. Matrix Can Contain 1000 ppm of Impurity

IMPURITY DETECTION AT INTERFACES



AUTORADIOGRAPHIC IMAGE OF Ni 63 TRACER DIFFUSION INTO COPPER GRAIN BOUNDARY

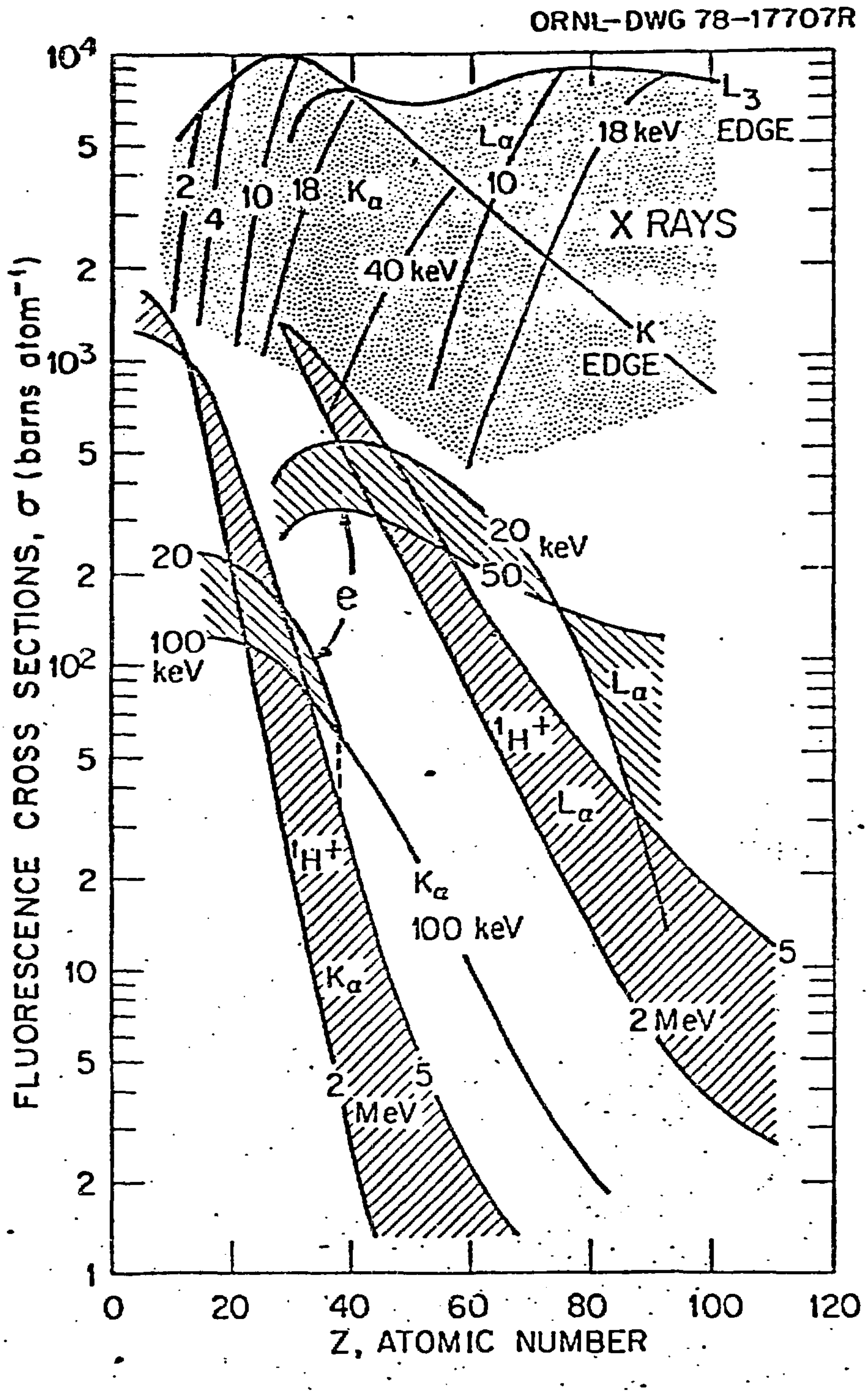


(a)

After T.J. Renouf

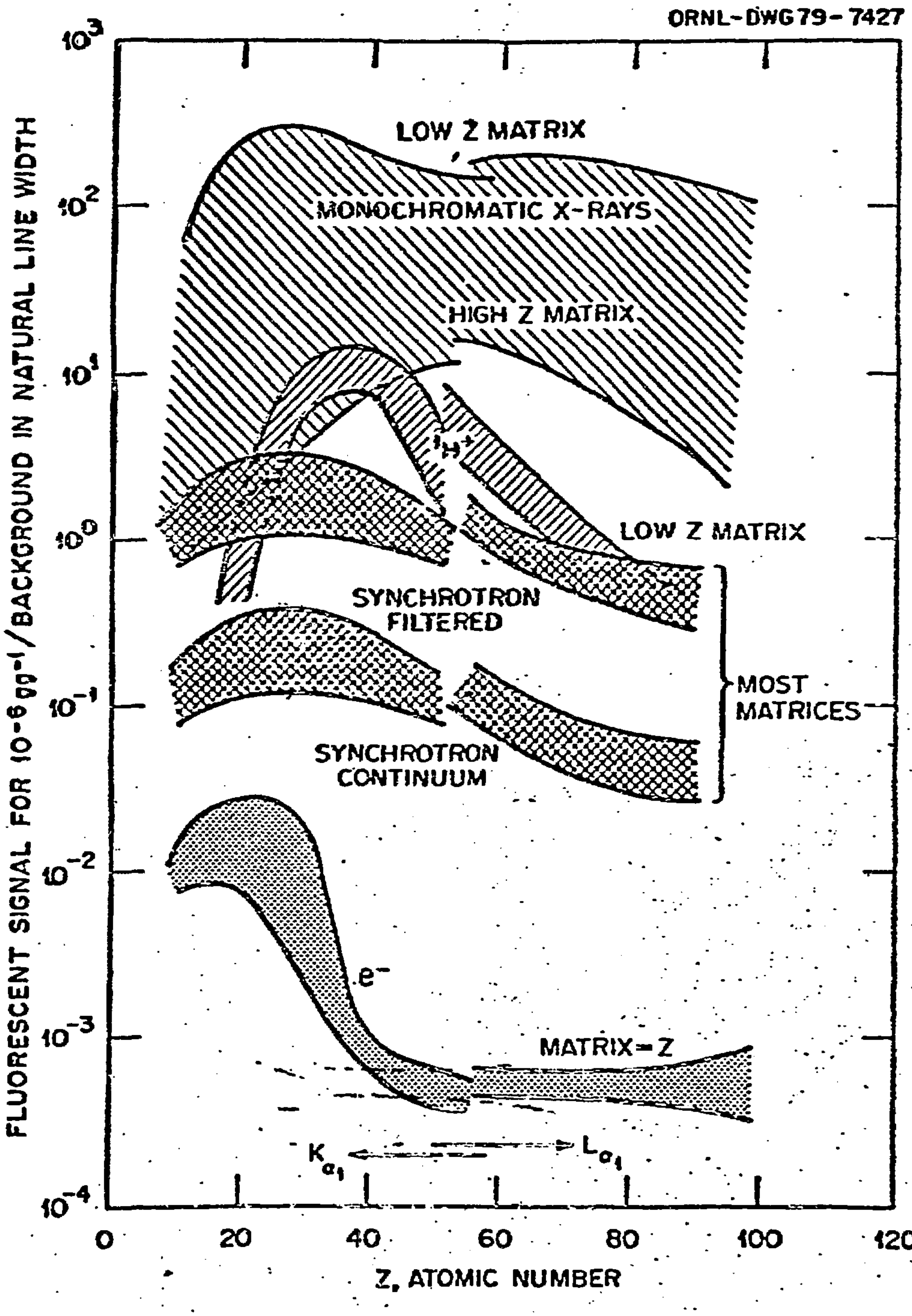
Synchrotron Radiation Research — C. J. Sparks, Jr.

Fig. 2 Top



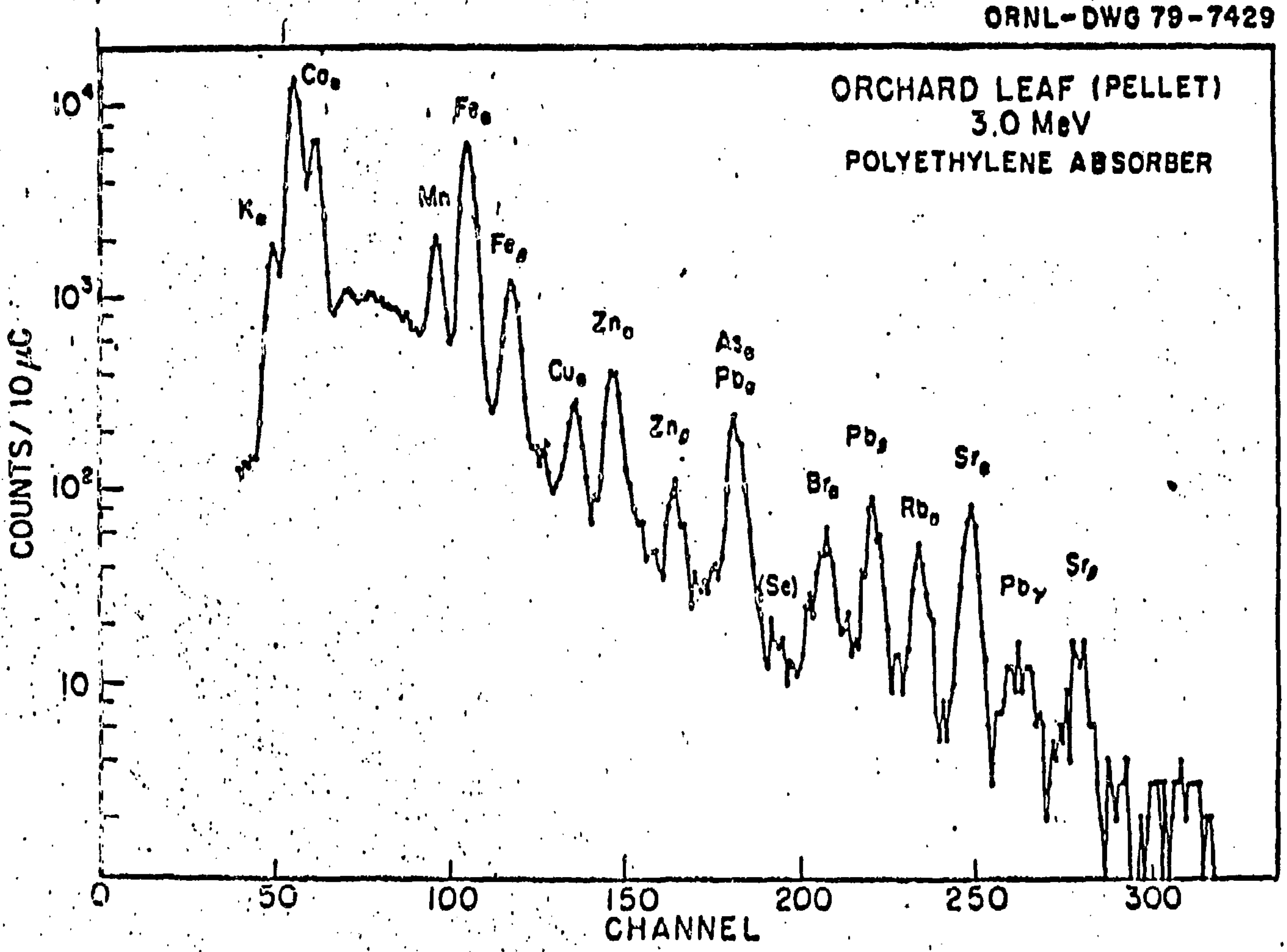
Synchrotron Radiation Research — C. J. Sparks, Jr.

Fig. 23 Top

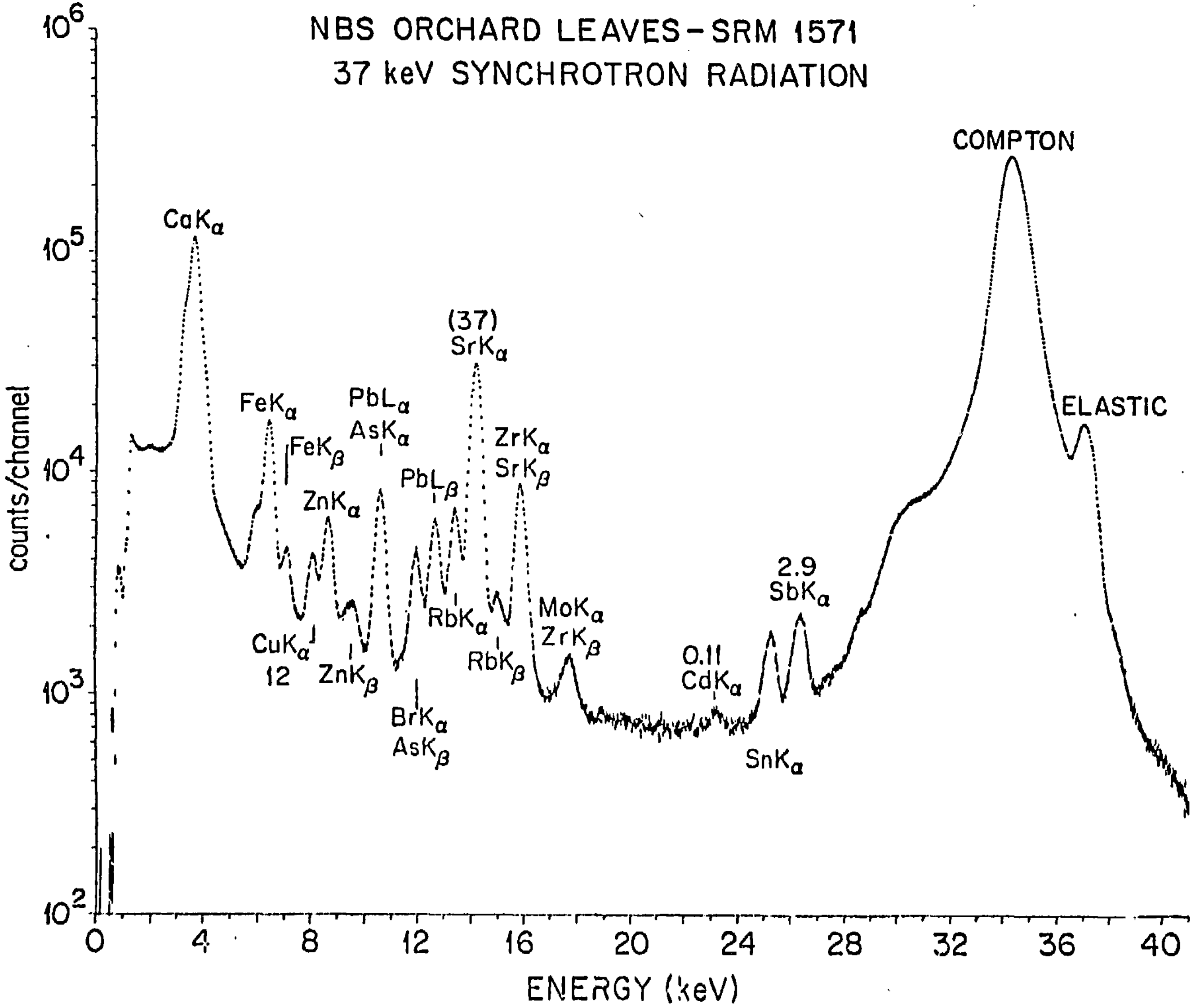


Synchrotron Radiation Research — C. J. Sparks, Jr.

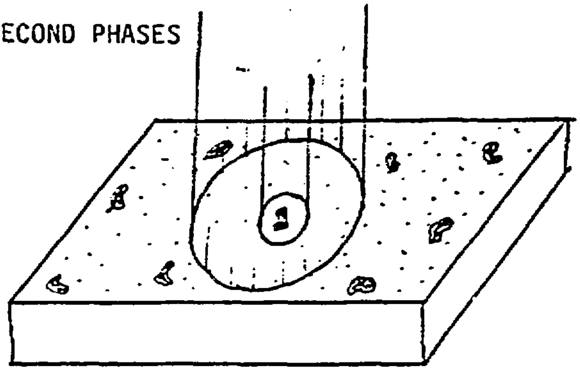
Fig. 11 Top



ORNL-DWG 77-11423R



SURFACE IMPURITIES AND SECOND PHASES



I. FLUORESCENT DETECTION

$$N_S \text{ (Signal Counts)} = \frac{I_o\,\sigma}{4\pi R^2}\begin{pmatrix}\text{Fluorescent}\\\text{Cross Section}\end{pmatrix}$$

$$N_S = \frac{10^{14}\ \text{p}}{\text{Sec}\ \mu\text{m}^2} \times 10^{-3} \times 5 \times 10^{-21}\ \frac{\text{cm}^2}{\text{Atom}} \times \frac{10^8\ \mu\text{m}^2}{\text{cm}^2} = \frac{10^{-2}\ \text{p}}{\text{Sec Atom}}$$

$$\frac{\text{Atoms}}{\mu\text{m}^2\ \text{Monolayer}} = \frac{10{,}000\ \text{Å} \times 10{,}000\ \text{Å}}{2.35\ \text{Å} \times 2.35\ \text{Å}} = 1.8 \times 10^7\ \text{Atoms}$$

$$N_S = \frac{10^{-2}\ \text{p}}{\text{Sec Atom}} \times 1.8 \times 10^7\ \text{Atoms} = \frac{1.8 \times 10^5\ \text{p}}{\text{Sec Monolayer}}$$

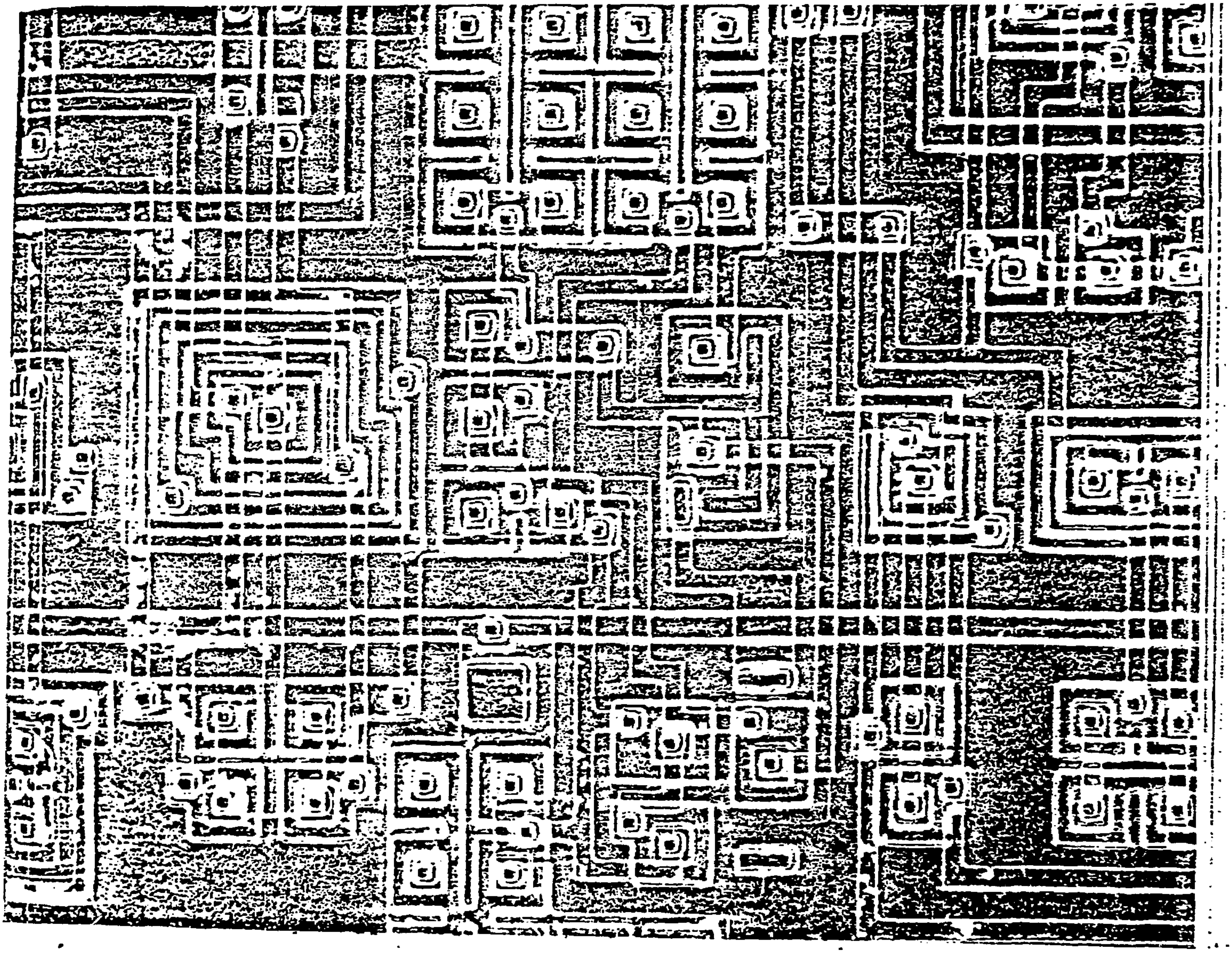
II. MINIMUM DETECTABLE LIMIT WITH μm^2 PROBE, $\tau = 1$ Sec

2.7×10^{-4} Monolayer
5×10^3 Atoms
40 Å-diam Particle

III. MINIMUM DETECTABLE LIMIT WITH 500 $Å^2$ PROBE, $\tau = 1$ Sec

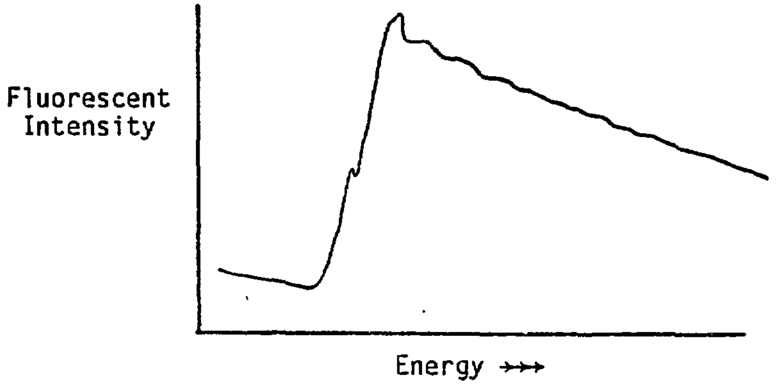
5.4×10^{-3} Monolayer
250 Atoms
15 Å-diam Particle

ELECTRONIC MICROCIRCUIT DEVICE RESEARCH WILL BENEFIT ENORMOUSLY FROM THE HIGH SENSITIVITY OF AN X-RAY MICROPROBE



CHEMICAL INFORMATION: EXAFS AND DIFFRACTION

I. EXAFS BY MEASURING FLUORESCENCE



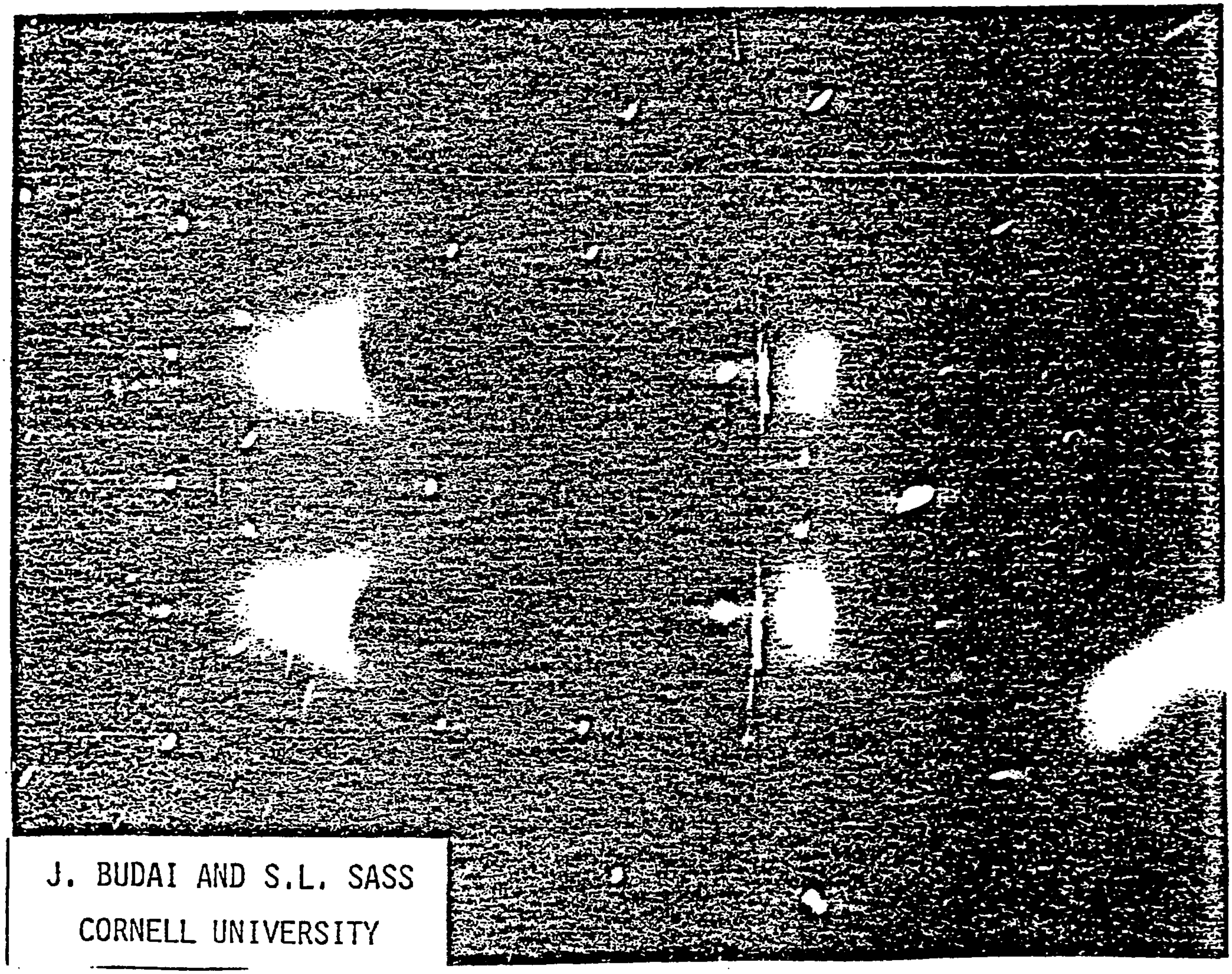
$$\left.\begin{array}{l}\text{Monolayer}\\ \quad\text{600 Å Particle}\\ \quad\text{84 ppm}\end{array}\right\}\ 1.8\times 10^{4}\ \frac{\rho}{\text{sec}}\ \text{for}\ \frac{10^{13}\ p}{\text{sec eV }\mu m^{2}}\ \text{Incident}$$

II. DIFFRACTION: MINIMUM DETECTABLE LIMIT

CRYSTALLINE	1 μm^2 Probe τ = 1 Sec	10^{-2} of a Monolayer 1.6 × 10^3 Atoms in a Particle 28 Å-diam Particle
AMORPHOUS	1 μm^2 Probe τ = 1 Sec	6 Monolayers
	500 Å^2 Probe τ = 1 Sec	1 × 10^6 Atoms 235 Å-diam Particle

DIFFRACTION PATTERN FROM

Au $\Sigma = 13$ ($\theta = 22.6°$) [001] TWIST BOUNDARY



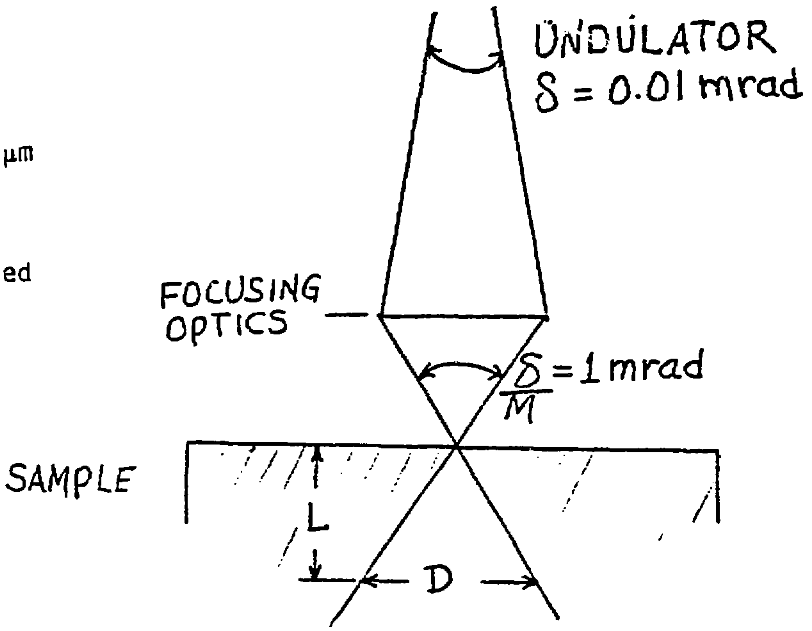
J. BUDAI AND S.L. SASS
CORNELL UNIVERSITY

BEAM PENETRATION AND DIFFRACTION LIMITATIONS FOR X-RAY MICROPROBE

I. BEAM PENETRATION:

$$L = \frac{D}{\delta} = \frac{1\ \mu m}{1\ mrad} = 10^3\ \mu m$$

With $L < 10^3\ \mu m$, $1 \mu m$
Probe Size Is Preserved



II. PROBE SIZE: Mag = 1/100, 2 μm × 8 μm

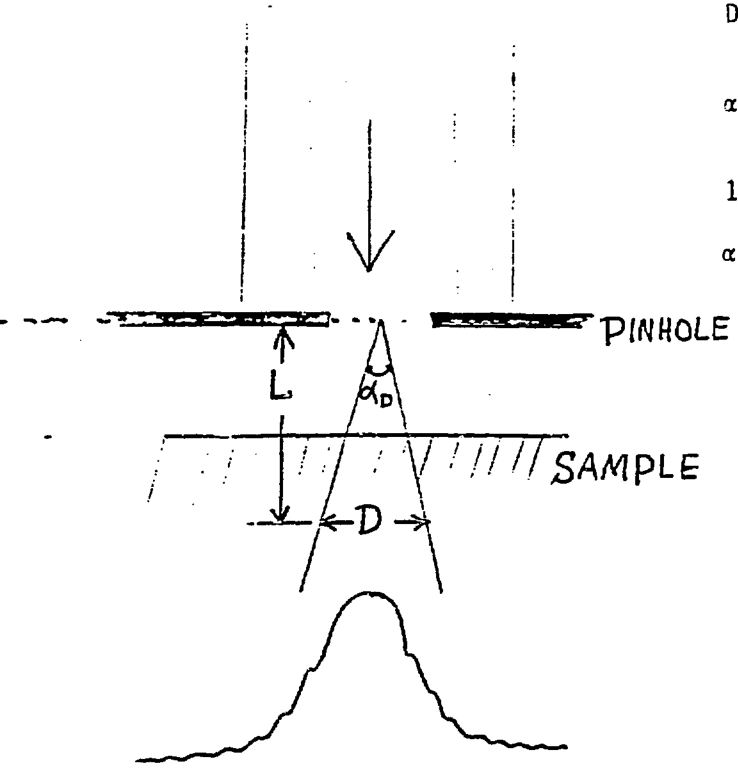
NEED PINHOLE COLLIMATION FOR < μm

DIFFRACTION LIMIT

$$\alpha_D\ mrad = \frac{0.244\ \lambda Å}{D_{\mu m}}$$

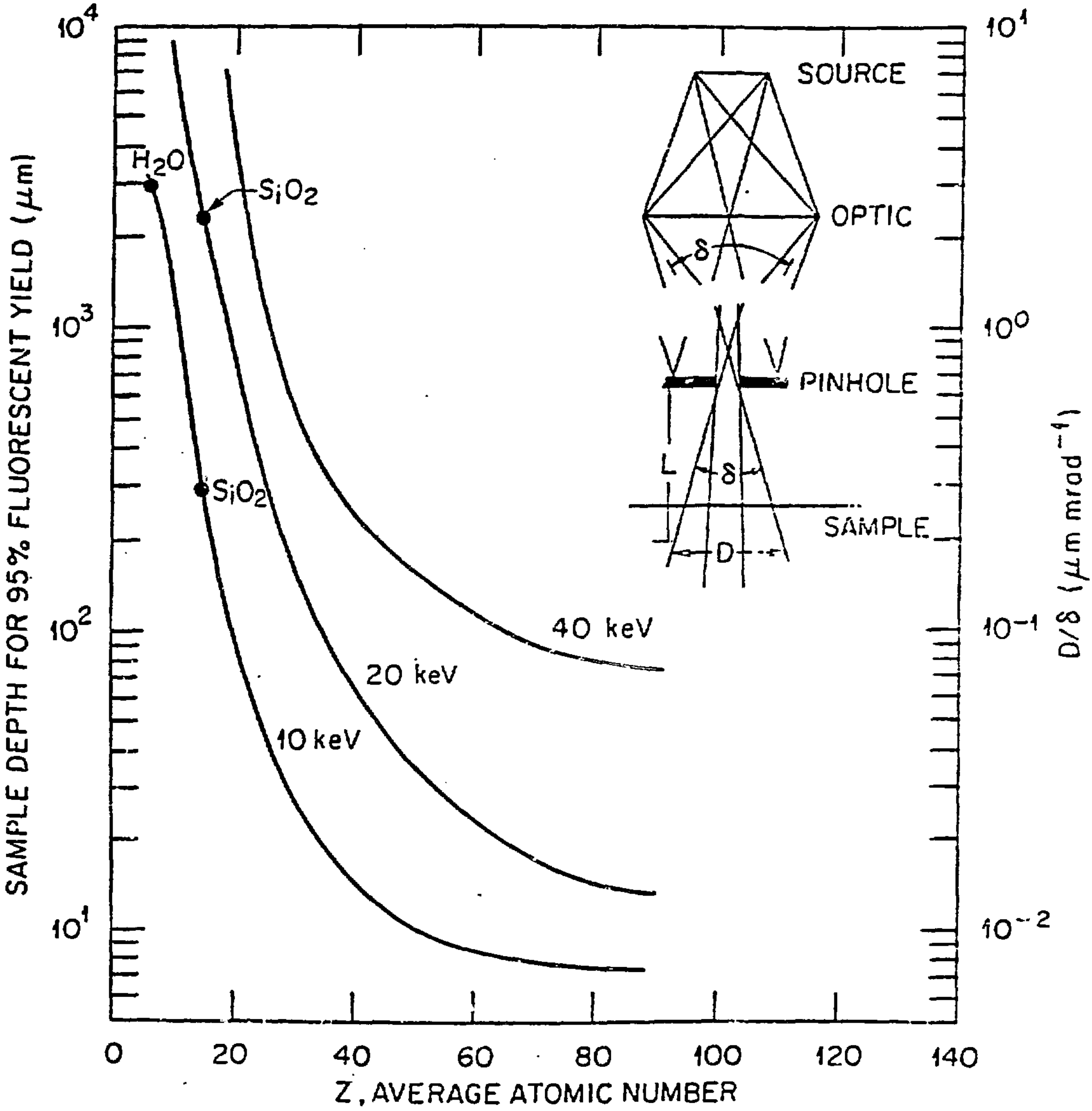
12.4 keV X-Ray and D = 500 Å,

$$\alpha_0 = 4.9\ mrad,\ and\ L = \frac{D}{\alpha_0} = \underline{\underline{10\ \mu m}}$$

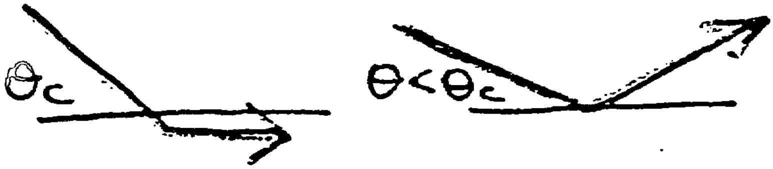


PENETRATION DEPTH OF X RAYS INTO MATERIALS FOR 95% OF THE FLUORESCENT YIELD

ORNL-DWG 83-16645R

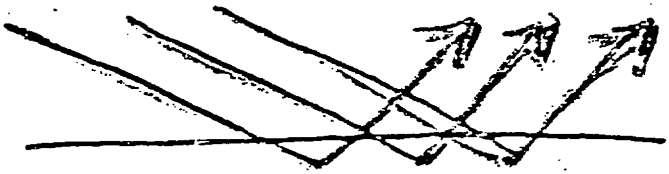


SURFACE PENETRATION OF X-RAYS CAN BE VARIED BY USING A GLANCING ANGLE GEOMETRY.



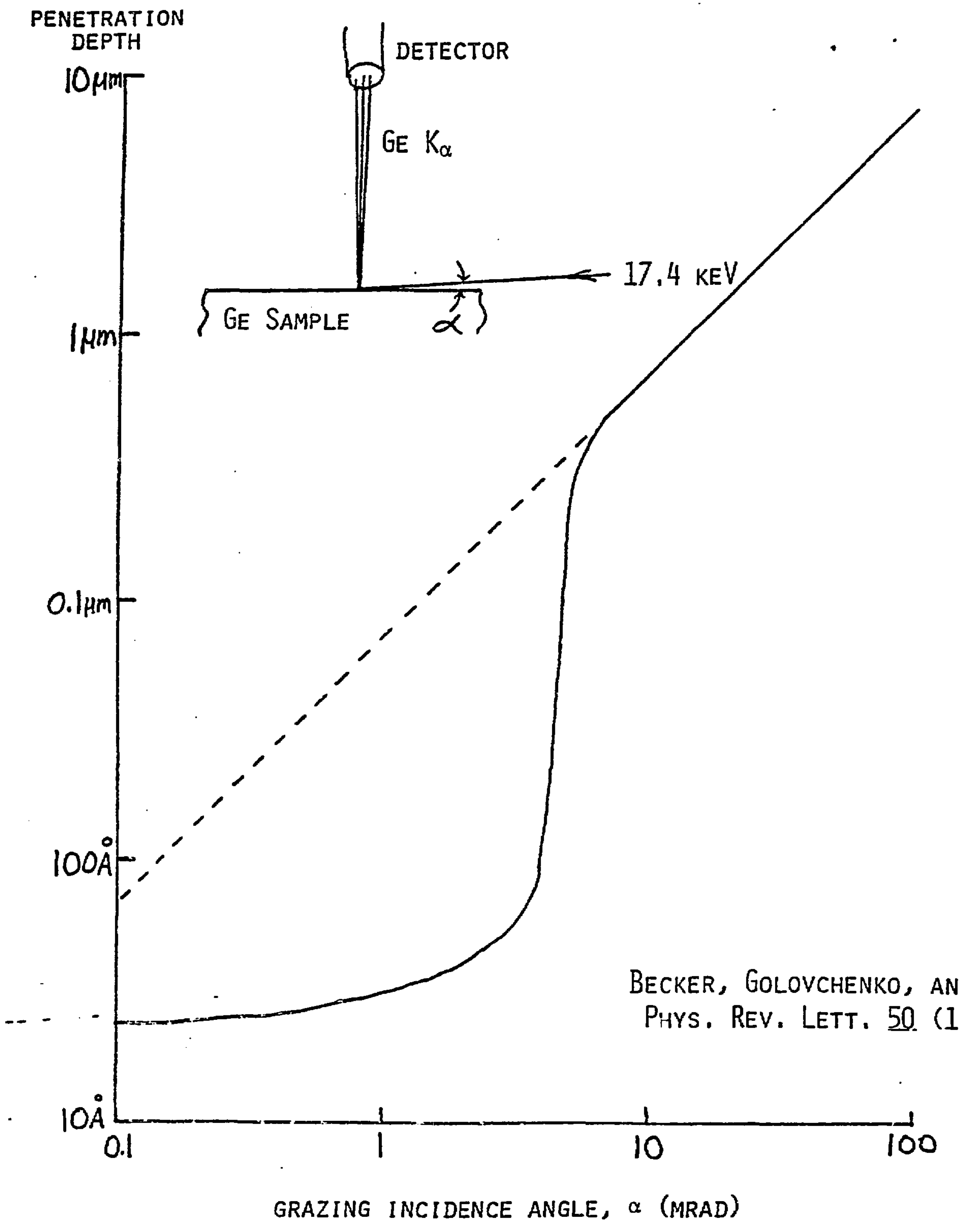
DEPTH OF PENETRATION DEPENDS ON ABSORPTION AND DENSITY OF SAMPLE, $\underline{\underline{\theta}}$!

(TYPICAL 50-1000 Å SKIN DEPTH)



$\sim$ 0-10 MRAD = θ_c HENCE SMALL OPENING ANGLE OF SYNCH. VITAL.

DEPTH PROFILING WITH DIFFRACTION AND FLUORESCENCE



Becker, Golovchenko, and Patel
Phys. Rev. Lett. 50 (1983)

I. GEOCHEMISTRY HAS SUPPLIED THE MAJOR PUSH FOR INSTRUMENTING AN X-RAY MICROPROBE AT THE NSLS.

- MEASUREMENTS OF TRACE ELEMENT CONCENTRATIONS AS A FUNCTION OF DISTANCE FROM SOURCE POINTS (SURFACE INTERFACES AND INCLUSIONS) COMBINED WITH CHEMICAL DATA WILL BRING NEW INFORMATION CHARACTERIZING THE TIMES, TEMPERATURES, PRESSURES, AND CHEMICAL ENVIRONMENT FOR RECONSTRUCTION OF THE GEOLOGICAL AGE AND CONDITIONS UNDER WHICH TERRESTRIAL AND EXTRA-TERRESTRIAL MATTER FORMED.

II. ENVIRONMENTAL SCIENCES AND BIOLOGY HAS INITIATED THE INSTRUMENTATION OF AN X-RAY MICROPROBE AT SSRL AND A PROPOSAL FOR ONE ON PEP.

X-RAY MICROPROBES BASED ON UNDULATORS IN A 6 GeV STORAGE RING WILL PRODUCE NEW INFORMATION: NOT JUST MORE OF THE SAME.

- MATERIALS DEFECTS AND IMPURITIES: MECHANICAL, CHEMICAL, AND ELECTRICAL PROPERTIES.
- CHEMISTRY, PHYSICS, MEDICINE, GEOCHEMISTRY, ENVIRONMENTAL: SYNERGISTIC EFFECT.
- 1 μM → 500 Å RESOLUTION IN THICK SAMPLES.
- PPB AND 10^{-5} MONOLAYER SENSITIVITY.
- OPERATES IN AIR, WATER: IN VIVO.
- 10^{-6} THE ENERGY DEPOSITED BY CHARGED PARTICLES FOR SAME MDL.