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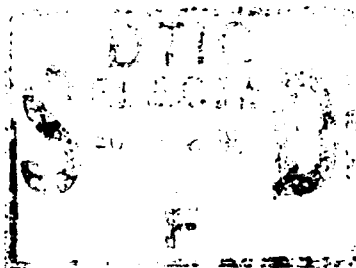


STRUCTURAL INTERMETALLICS

PERSPECTIVES ON SCIENCE AND TECHNOLOGY

February 5 & 6, 1994

**DEFENCE METALLURGICAL RESEARCH LABORATORY
HYDERABAD
INDIA**



Vol. II

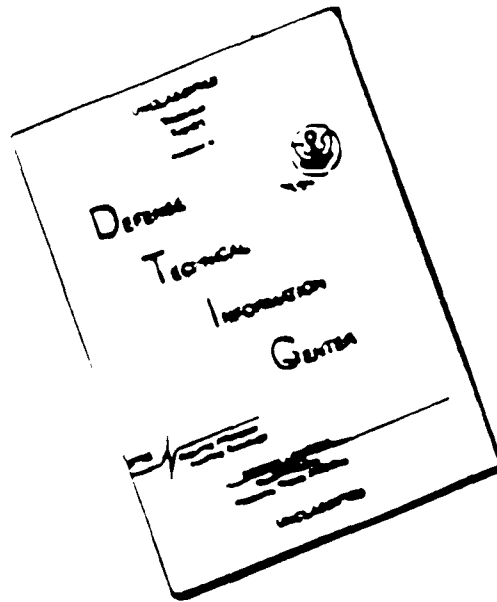
**Metals Group,
MATERIALS RESEARCH SOCIETY OF INDIA**

**ASIAN OFFICE OF AEROSPACE RESEARCH & DEVELOPMENT
US Air Force**

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FOREWORD

A two day symposium on "Structural Intermetallics - Perspectives on Science and Technology" was held at the Defence Metallurgical Research Laboratory, Hyderabad, India on February 5 and 6, 1994, preceding the Annual General Meeting of the Materials Research Society of India. The Symposium was organised by the Metals Group of the Materials Research Society of India and co-sponsored by the Asian Office of Aerospace Research and Development, US Air Force. C.V.Sundaram, Chairman, Metals Group of the Materials Research Society of India noted in his introductory remarks that the progress towards the development of intermetallics to application has been 'exasperatingly' slow. Robert Cahn of the University of Cambridge, UK, in a keynote lecture provided a historical perspective on early research on 'weakly ordered' alloys and examples of more recent work on 'strongly ordered' compounds.

The symposium featured ten overview talks. Dan Miracle of Air Force Wright Laboratory addressed both science-based issues and engineering concerns related to the metallurgy of NiAl. He noted that NiAl could be significantly strengthened to the levels of several superalloys and, in any case, possessed a variety of attractive properties such as low density, high thermal conductivity and excellent environmental resistance. Nevertheless, a reasonable combination of toughness and high temperature strength continues to be an elusive goal, and the current approach emphasises design methodologies which can use low toughness materials with adequate factors of safety. The alloy system presents large opportunities for research in fabrication (casting technology), strengthening and deformation behaviour. Vinod Sikka presented the status of Fe_3Al and Ni_3Al from an applications engineering perspective with emphasis on work at the Oak Ridge National Laboratory, USA. He stressed specially the excellent corrosion and sulphidation resistance of the Fe_3Al base alloys and their cost benefits in relation to stainless steel. High temperature strength levels continue to be of concern and strong environmental effects on ductility at room temperature have been identified. It appears unlikely that Ni_3Al base alloys will find aeroengine applications, but their excellent carburisation resistance and high temperature strength lend them to applications in heat treatment furnaces, automotive vehicles and in manufacturing. Cost is a key concern in these applications. A summary of the work on Ti_3Al and Ti_2AlNb base alloys at the Defence Metallurgical Research Laboratory, with emphasis on the key issues that limit application, was provided by Ashok Gogia. He described microstructural and compositional effects on primary creep in some detail emphasising that this area has not received adequate attention

in the literature, although the major contribution to creep strain arises from transient behaviour. Other drawbacks relate to oxygen induced dynamic embrittlement over the range of application temperatures and poor burn resistance, a feature common to all titanium alloys with the exception of TiAl. Patrick Martin from Rockwell Science Centre, USA described the current status on TiAl. Successful engine ground tests at General Electric of cast Ti-47Al-2Cr-Nb offer a positive outlook for application of an intermetallic alloy in rotating applications. His talk emphasised issues related to thermomechanical processing of these alloys as they affect microstructure evolution and emphasised the need to refine the processing-microstructure-property envelope in full scale ingot conversion and the development of low cost processing approaches for potential automotive applications.

Work on molybdenum disilicide was covered in two presentations : Dallis Hardwick summarised the physical metallurgy of MoSi₂ and described in some detail Rockwell Science Centre work on this material, while Sadananda from the Naval Research Laboratory, USA concentrated on the effect of SiC particulates and whisker composites with MoSi₂ on creep resistance. While composite microstructure can be designed to provide creep resistance much superior to superalloys and approaching ceramic-ceramic systems at temperatures greater than 1000°C, it was clear that low temperature toughness must be enhanced, perhaps utilising ductile phase toughening or laminate design. Two approaches to the stability of intermetallics were described by Raju from Indira Gandhi Centre for Atomic Research, India, and Ashok Singh from the Defence Metallurgical Research Laboratory, India. Raju described the variety of semi-empirical approaches using alloy theory parameters and concluded with his own work in developing a new structure map parameter which offers advantages over the Pettifor scheme. Ashok Singh offered a description of a variety of thermodynamic approaches including CVM to developing ground state structures in ordered hexagonal systems. Tassaduq Khan of ONERA, France described the nature and substance of European Community Schemes such as BRITE-EURAM, COST and CEASI as related to intermetallic programmes and provided a summary of ONERA work on B2 alloys based on the Ti-Al-Nb system and approaches to TiAl alloy development.

A variety of contributed presentations from various research groups in India covered work on phase transformations in TiAl, Zr₃Al and B2-DO₃ systems, powder metallurgy and ingot approaches to processing Fe₃Al and Al₃Ti alloys, the mechanical behaviour of alloys of the Ti₃Al-Nb system and oxidation resistance of Ti₃Al alloys. A dominant metallurgical theme that emerged from the symposium was the dichotomy that exists between high temperature strength and low temperature ductility in the

intermetallics. Alloying and processing schemes that enhance the one, almost inevitably do so at the expense of the other.

A hard copy of the material presented in the overview talks is provided in two volumes. The first covers the aluminides : NiAl, TiAl, Ni₃Al, Fe₃Al and Ti₃Al. The second presents the material on European intermetallic activities, molybdenum disilicide and its composites, the ground state structures and stability of intermetallics.

March, 1994

D. Banerjee
Defence Metallurgical Research Laboratory
Hyderabad-500258, India

PROGRAMME

Saturday, Feb 5

- 9.00 - 9.45 Intermetallics - The Fashionable and Unfashionable *R.W.Cahn*
University of Cambridge, U.K.
- 9.45 - 10.15 Coffee
- 10.15 - 11.00 Understanding and Applications of NiAl *D.B.Miracle* Air Force Wright
Laboratory, USA
- 11.00 - 11.45 Technology and Applications of Ni₃Al-Based Materials *V. K. Sikka*
Oakridge National Laboratory, USA
- 11.45 - 12.05 Development of Cold Rolling Texture in Ni₃Al (B) *R.K.Ray* Indian
Institute of Technology, Kanpur, India
- 12.05 - 12.25 Recrystallisation of Ni₃Al *A.K.Jena* Indian Institute of Technology,
Kanpur, India
- 12.25 - 1.15 Lunch
- 1.15 - 2.00 Promise versus Reality for High Temperature Applications of Gamma TiAl
- A Perspective *P.L.Martin* Rockwell Science Centre, USA
- 2.00 - 2.20 Diffusional Composition Invariant and Coarsening Phase Transformations
in TiAl Base Alloys *R.V.Ramanujam* Bhabha Atomic Research Centre,
Bombay, India
- 2.20 - 2.40 Interface Modification in two phase ($\gamma + \alpha_2$) Titanium Aluminide by Ternary
Additions and their Deformation Behaviour *S.R.Singh* National
Metallurgical Laboratory, Jamshedpur, India
- 2.40 - 3.15 Tea
- 3.15 - 4.00 The Stability of Intermetallics *S.Raju* Indira Gandhi Centre for Atomic
Research, Kalpakkam, India
- 4.00 - 4.45 Ground State Structures of Ordered Alloys *S. Lele & A.K.Singh*
Banaras Hindu University, Varanasi, India

Sunday, Feb 6

- 9.00 - 9.45 European Intermetallic Activities - Contributions from France *T. Khan*
ONERA, France
- 9.45 - 10.15 Coffee
- 10.15 - 11.00 Composites Based on Molybdenum Silicide : Progress and Prospects *D.A. Hardwick* Rockwell Science Centre, USA
- 11.00 - 11.45 Technology and Applications of Fe₃Al-based materials *V.K. Sikka* Oak Ridge National Laboratory, USA
- 11.45 - 12.05 Preparation and Processing of Fe₃Al Strips through Ingot and P/M processing *S.Bagchi, S.Suwas, S.Bhargava, S.Sangal and R.K.Dube* Indian Institute of Technology, Kanpur, India
- 12.05 - 12.25 Anti-phase boundaries in B2 and DO₃ Fe-Al-X (X=Cr, Mo) and DO₂₂/L1₂ Al-Ti-Ni Intermetallics *Ujjwal Prakash* Defence Metallurgical Research Laboratory, Hyderabad, India
- 12.25 - 12.45 Improvement in Mechanical Properties of Iron Aluminides *Aruna Bahadur* National Metallurgical Laboratory, Jamshedpur, India
- 12.45 - 2.00 Lunch
- 2.00 - 2.45 The Metallurgy of Ti₃Al Base alloys *A.K.Gogia* Defence Metallurgical Research Laboratory, Hyderabad, India
- 2.45 - 3.05 Low Cycle Fatigue Behaviour of Ti-27Al-15Nb *P.N.Singh, B.K.Singh, C.Ramachandra and V.Singh* Banaras Hindu University, Varanasi, India
- 3.05 - 3.25 High Temperature Oxidation of Ti₃Al *T.K.Roy, R.Balasubramaniam and A.Ghosh* Indian Institute of Technology, Kanpur, India
- 3.25 - 4.00 Tea
- 4.00 - 4.20 Morphological Features of Ti₃Al Based Intermetallic Alloys Prepared by Reaction Synthesis *M.Sujata, S.Bhargava and S.Sangal* Indian Institute of Technology, Kanpur, India
- 4.20 - 4.40 Phase Transformations in Zr₃Al Base Alloys *R.Tewari, G.K.Dey and P.Mukhopadhyay* Bhabha Atomic Research Centre, Bombay, India

**3. European Intermetallics Activities and
Contribution from France
T.Khan and S.Naka
ONERA, France**

European Intermetallics Activities and Contribution from France

T. KHAN and S. NAKA

ONERA, 29, Av. de la Division Leclerc, 92322 Châtillon, France

February, 5-6, 1994, Hyderabad

Principal European Programme on Advanced Materials

- 1) BRITE/EURAM
- 2) COST 513
- 3) CEASI

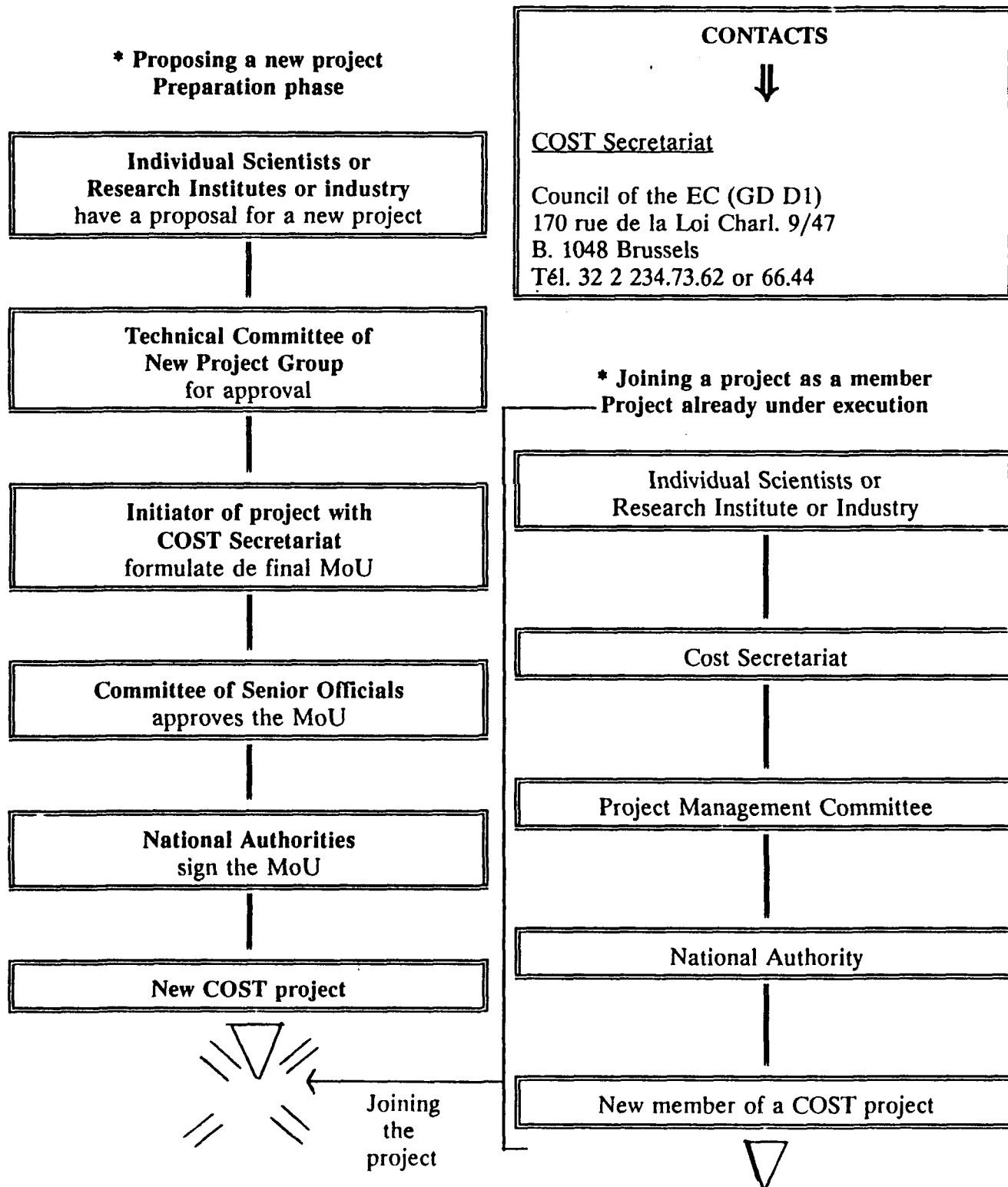
BRITE - EURAM

TABLE 1: GENERAL CONDITIONS FOR PARTICIPATION

Type 1 Projects (up to 90% of available budget)		
Industrial Applied Research -indicative Priority Themes -precompetitive and collaborative -potential for exploitation -subsequent development expected	Size	-10 Man-years minimum -1 to 3 Mecu
	Duration	-2 to 4 years
	Partners	-at least 2 independent industrial enterprises -at least 2 different Member States
Type 2 Projects (7% to 10% of available budget)		
Focused Fundamental Research -upstream of Type 1 -indicative Priority Themes -precompetitive and collaborative -industrial endorsement from 2 Member States	Size	-10 Man-years minimum 0.4 to 1 Mecu
	Duration	-2 to 4 years
	Partners	-at least 2 organisations -at least 2 different Member States
Co-ordinated Activity		
Co-ordination of related research -within Technical Areas -in different Member States -co-ordination activities only -proposers must justify activity	EC Funding	-up to 100% coordination costs -not research costs
	Partners	-as appropriate
	Calls	-continuous

C O S T

PRESENTING NEW PROPOSALS & JOINING PROJECTS Flow Charts on Project Procedures

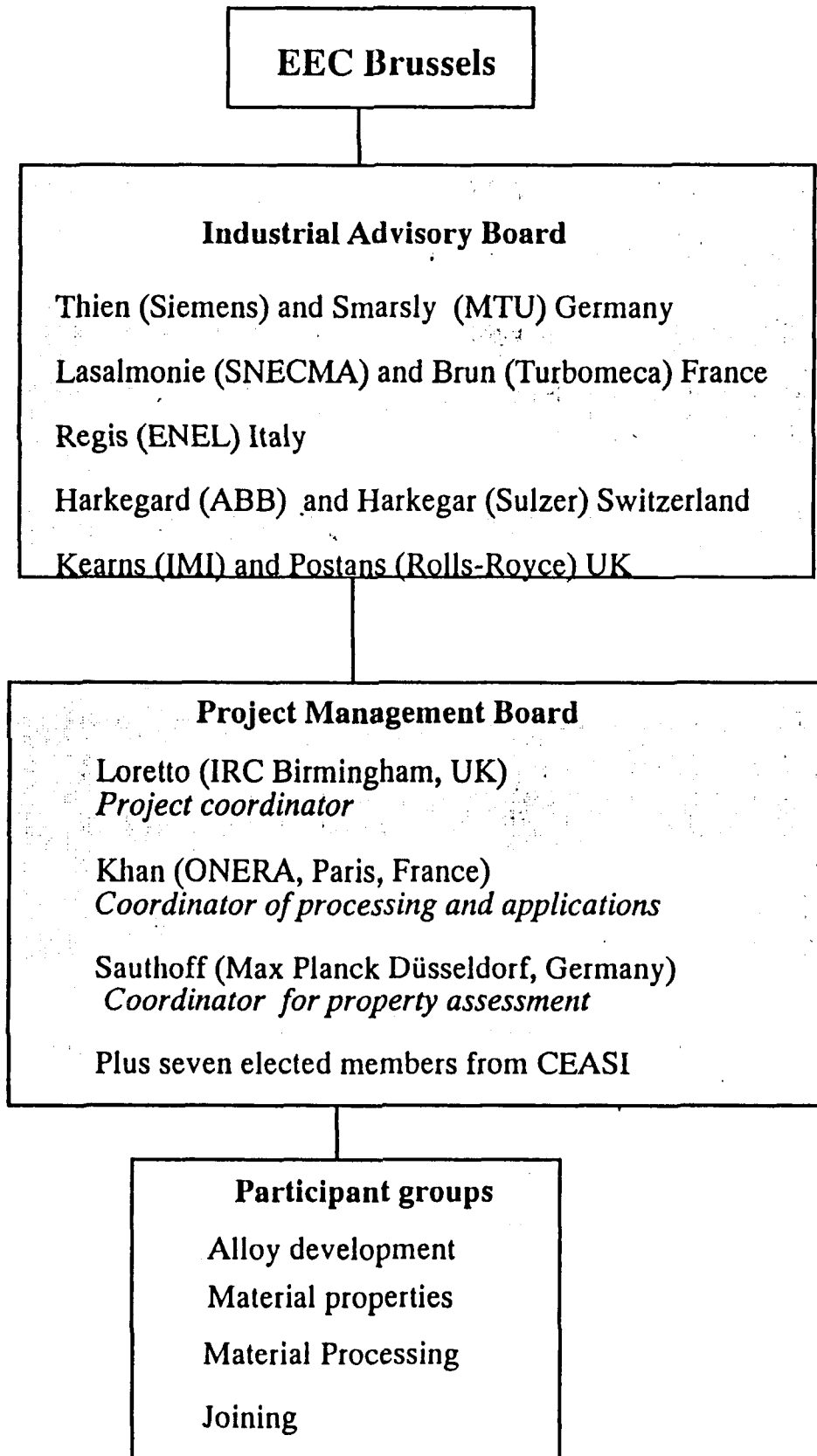


Concerted European Action on Structural Intermetallics (CEASI)

The objectives of CEASI are:

- (i) To provide a framework by which a coherent pre-competitive research programme can be carried out in the field of structural intermetallic-based alloys.**
- (ii) To ensure that there is a balance of activity in the research programme across the whole discipline, so that European intermetallics research goes ahead in a well-balanced way.**
- (iii) To supply, process and circulate reference materials to participants.**
- (iv) To develop a fundamental understanding of alloying behaviour in intermetallics so that alloy development and alloy processing is on a firm basis for future application to the manufacture of components.**

CEASI Project Management



French Programmes

- Various Intermetallics
 - Ti_3Al (or Ti_2AlNb) and Nb-base intermetallic alloys
 - TiAl
 - NiAl
 - Ni_3Al
 - Fe_3Al and FeAl
 - Two-phase A2+B2 alloys
- Interaction with the industry
SNECMA, Turboméca, Aérospatiale Dassault and SEP
- Formation of a GDR (research group)
Basic research oriented

Ti₃Al or Ti₂AlNb base

High Niobium Titanium Aluminides (B2)

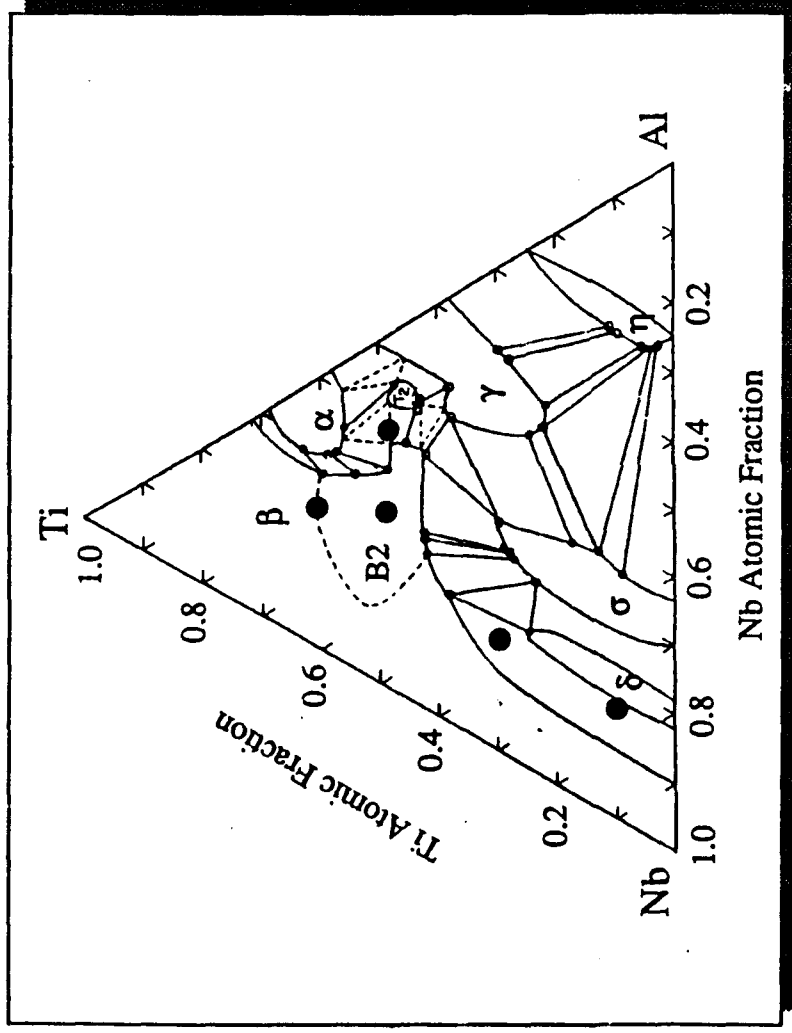
Increasing Nb beyond 25 at. %

Advantages

- Fine microstructure $\Rightarrow$ yield stress
- Higher amount of ordered β phase
 - $\Rightarrow$ high temperature strength
 - $\Rightarrow$ room temperature ductility
- Orthorhombic phase $\Rightarrow$ room temperature ductility

Disadvantage

- High density (> 5)



Compositions of alloys of the Ti-Al-Nb system in which the B2 phase was observed. They were plotted in the phase diagram of the Ti-Al-Nb system (Isothermal section at 1200°C), proposed by Perepezko et al. (1990).

TiAl base

Activities on $\gamma+\alpha_2$ TiAl-based Alloys

- Effect of various alloying elements
Fe, Cr, Mo, W : γ -stabilizing
Nb, Ta : α_2 -stabilizing
⇒ Development of new compositions
- Thermomechanical processings (isothermal forging and extrusion)
e.g. on $\text{Ti}_{48}\text{Al}_{48}\text{Nb}_2\text{Cr}_2$
 - microstructure control before and after processing
- Casting : e.g. on TiAl-Fe-V-B
 - good castability : addition of B? and/or β -phase solidification?
- Powder metallurgy
 - reactive sintering
- Basic study on phase transformation mechanisms

Key Metallurgical Factors

ONERA

- Alloy composition
 - Some beneficial alloying elements identified
- Microstructure
 - Lamellar structure : most frequent and important
 - Various microstructures resulting from various phase-transformation sequences
- ✓ • Texture
 - Solidification texture often extremely pronounced
- Porosity
 - Macro- and micro-porosities
- ✓ • Impurity level
 - High purity materials required
- Machining
 - Good quality of the surface

Texture

During solidification

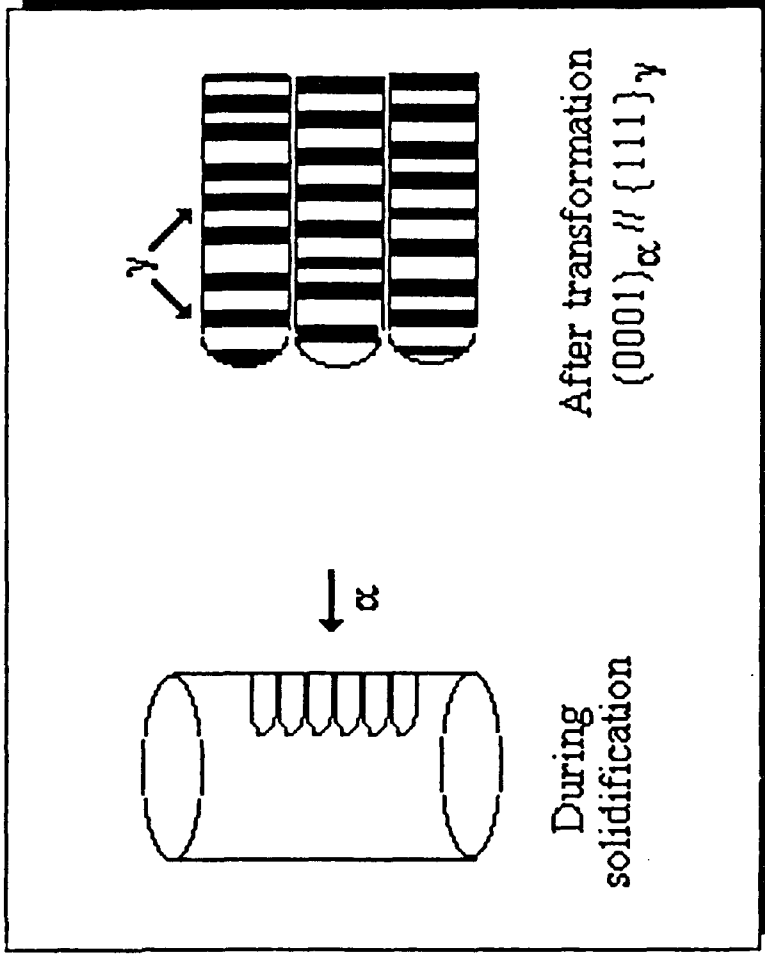
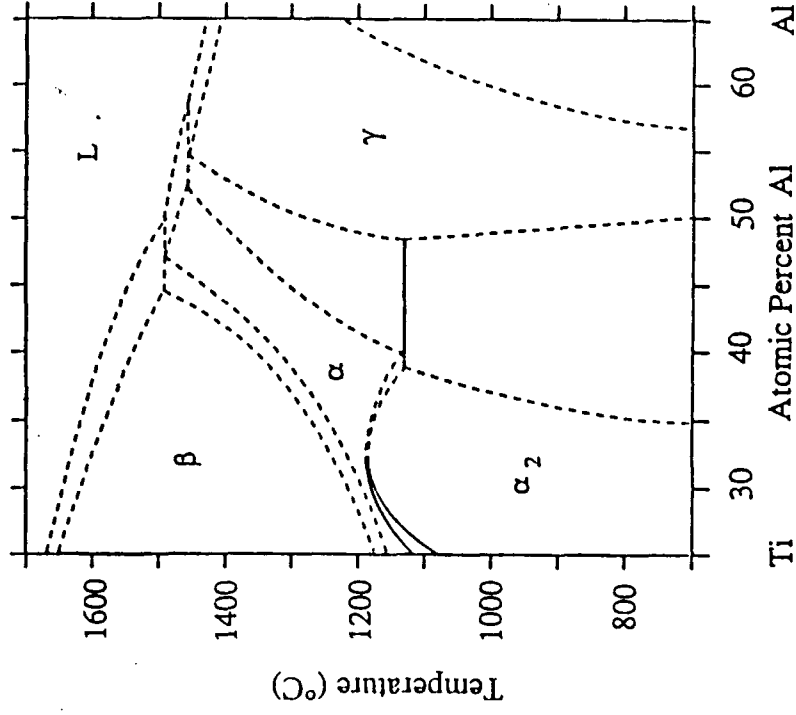
$L \Rightarrow \alpha$

α : HCP $\Rightarrow$ crystal growth direction $//$ [0001]

During the formation of lamellar structure

$\alpha \Rightarrow \alpha + \gamma \Rightarrow \alpha_2 + \gamma$ (or $\alpha \Rightarrow \alpha_2 \Rightarrow \alpha_2 + \gamma$)

(0001) α or $\alpha_2 //$ {111} γ

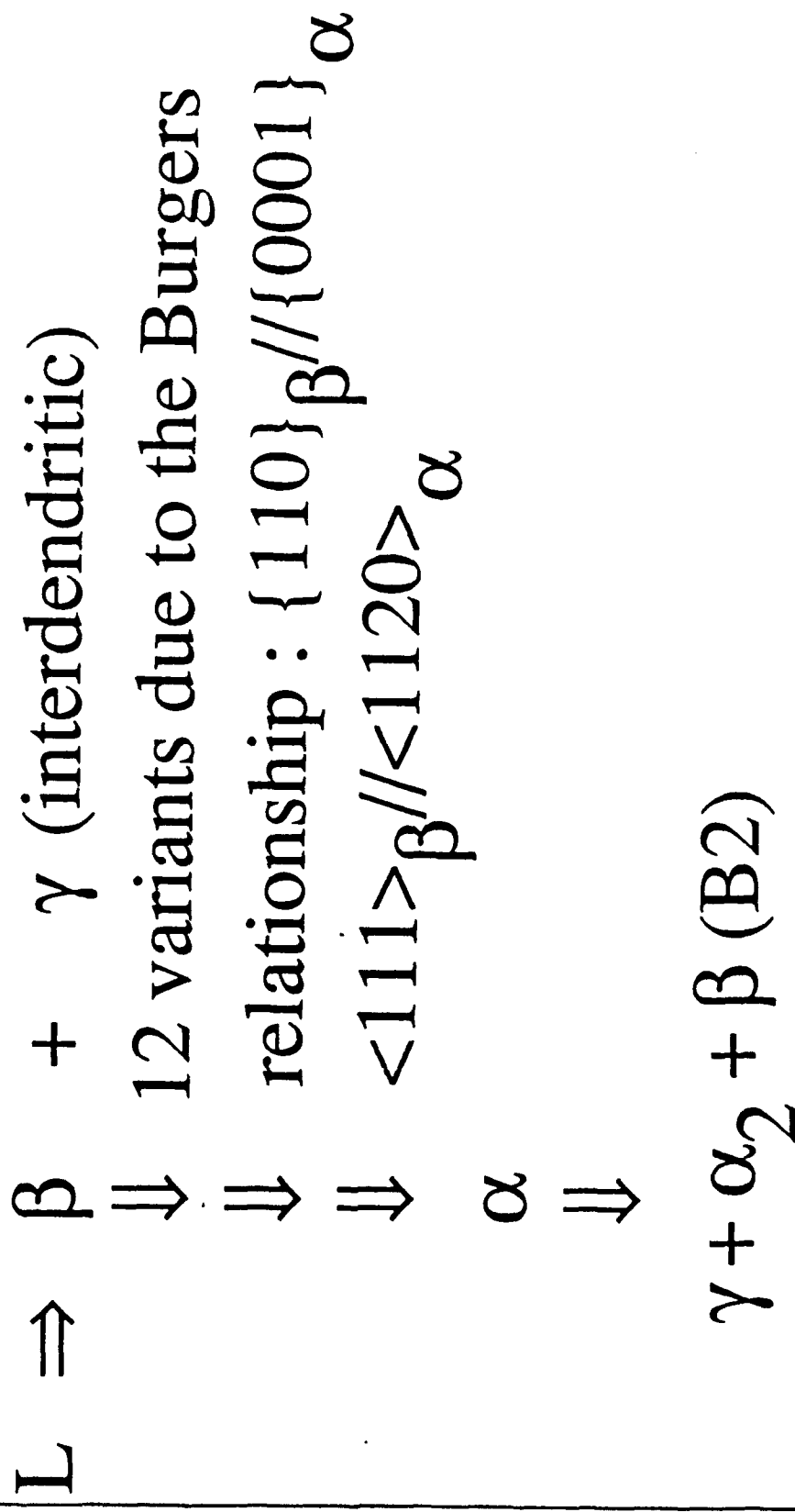


Acute solidification texture
⇒ scattering of mechanical properties data

Future directions in the research activities related to the texture

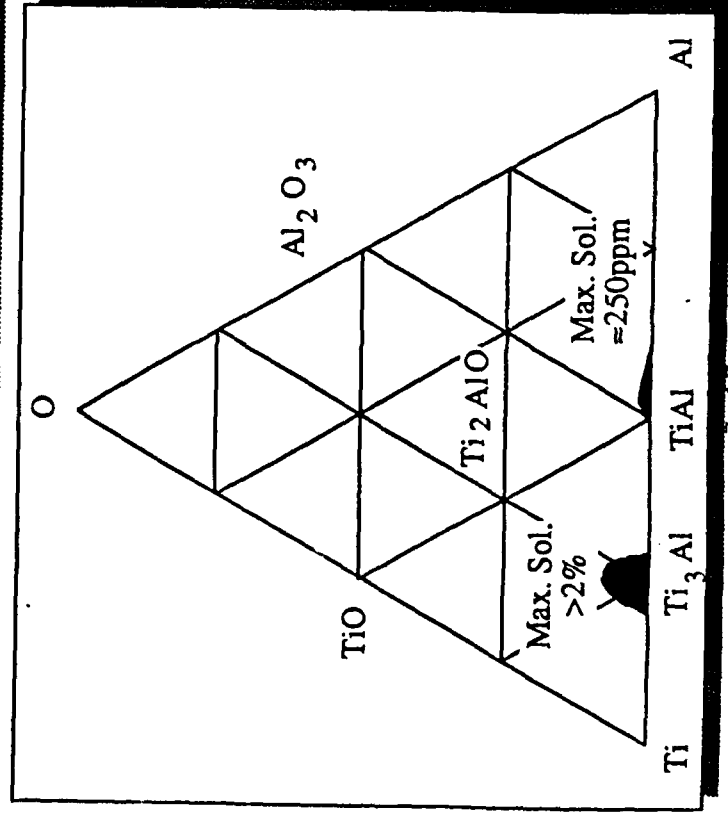
- Investigate the evolution of texture during thermal and thermomechanical processings
⇒ reduce or suppress the solidification texture
- Identify suitable alloy compositions to promote solidification with the β phase ⇒ weaker texture

Phase transition sequence



Impurity level

- Atom-probe analysis of the two phases γ and α_2 in the lamellar structure
Maximum solubility of oxygen is very low : $\approx 300 \text{ at. ppm}$.
- Tentative explanation of the origin of a better ductility of $\gamma + \alpha_2$ two-phase alloys, compared to γ single-phase alloys
 - in two-phase alloys : oxygen is "dispersed" throughout the α_2 lamellae.
 - in single phase : oxygen is strongly segregated in the form of oxide.



3.17

Composition determined by Chemical Analysis and
Volume Fraction of the α_2 Phase estimated through TEM.

	Ti ₅₂ Al ₄₈	Ti ₅₄ Al ₄₆
Aluminium	47.9±0.4 at. %	46±0.4 at. %
Titanium	51.8±0.4 at. %	53.7±0.4 at. %
Oxygen	2290±230 at.ppm	2505±250 at.ppm
F _v α_2	10±5%	30±5%

Oxygen Concentrations as well as Volume Fractions
of the α_2 Phase deduced from Atom-Probe Analysis.

	Ti ₅₂ Al ₄₈		Ti ₅₄ Al ₄₆
	α_2	$\gamma =$	$\gamma =$
<u>Oxygen</u>	19200±1200 at.ppm	230±70 at.ppm	8100±700 at.ppm
F α_2	10 ±2%		29 ±7%

Future directions in the research activities related to the impurity level

- Prepare two phase $\gamma+\alpha_2$ alloys containing less than 250 at.ppmO (≈ 100 wt.ppmO)
- Investigate their deformation behaviour
 - $\Rightarrow$ change in plastic deformation mechanisms ?
mobility of $1/2<110]$ and $1/2<112]$ dislocations
 - $\rightarrow$ influence on macroscopic ductility ?

Various transformation modes

1) Formation of lamellar structure

- $\alpha \Rightarrow \alpha + \gamma \Rightarrow \alpha_2 + \gamma$ or $\alpha \Rightarrow \alpha_2 \Rightarrow \alpha_2 + \gamma$
- nature of various interfaces :

γ/α_2 and γ/γ (TB's, ODB's, PTB's, MB's)

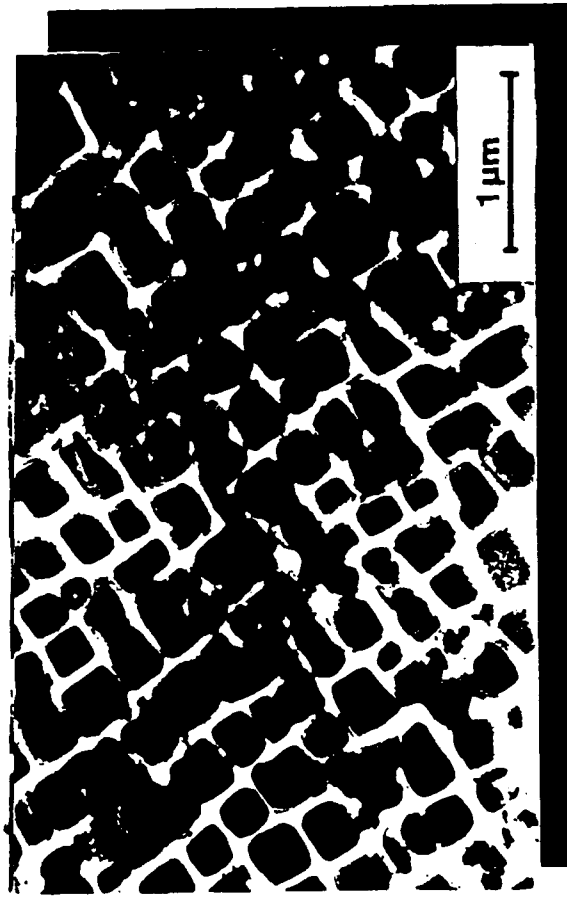
2) Massive transformation

- $\alpha \Rightarrow \gamma$
- numerous defects and interfaces including γ APB's

3) Discontinuous coarsening of γ lamellae

- solute redistribution through moving grain boundaries ?
- mechanism less clarified

Two-Phase Systems

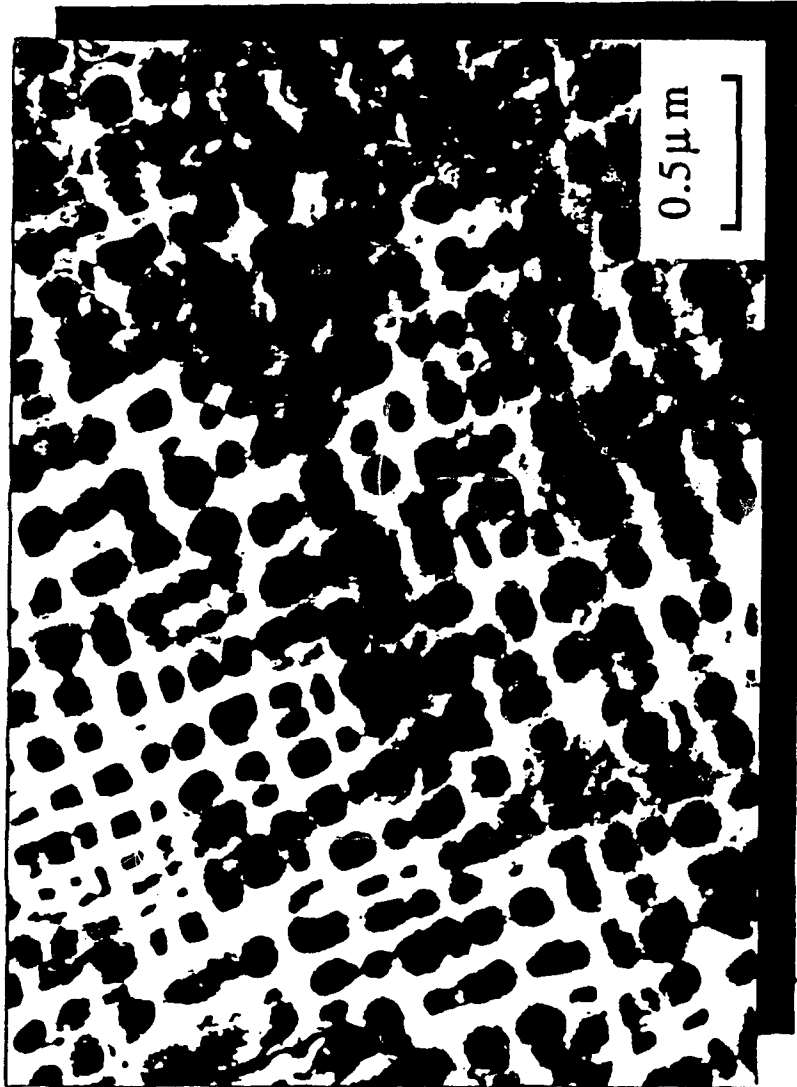


γ - γ' microstructure
(Ni-base superalloy)

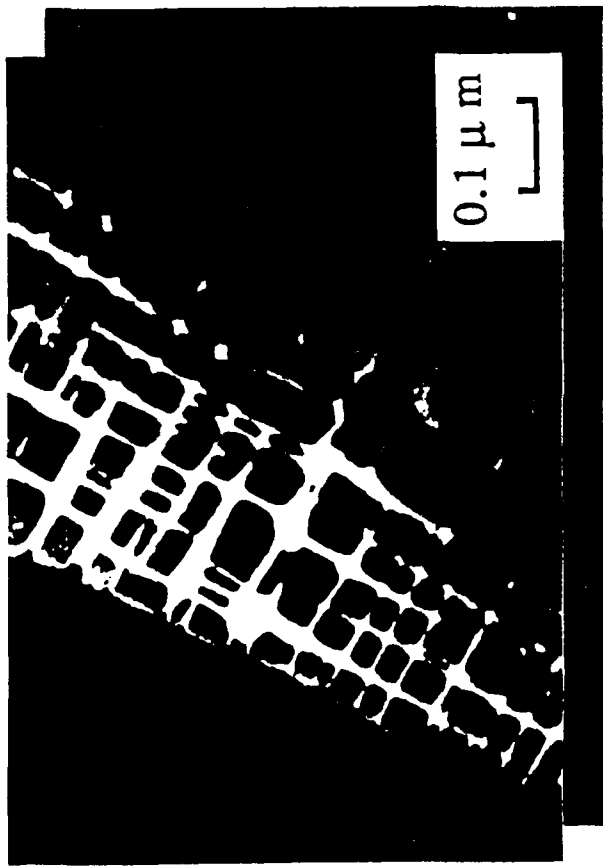
Two-phase A2+B2 (or A2+L2₁) alloys (γ - γ' type microstructure)

Nb base, Ta base, Fe base etc.

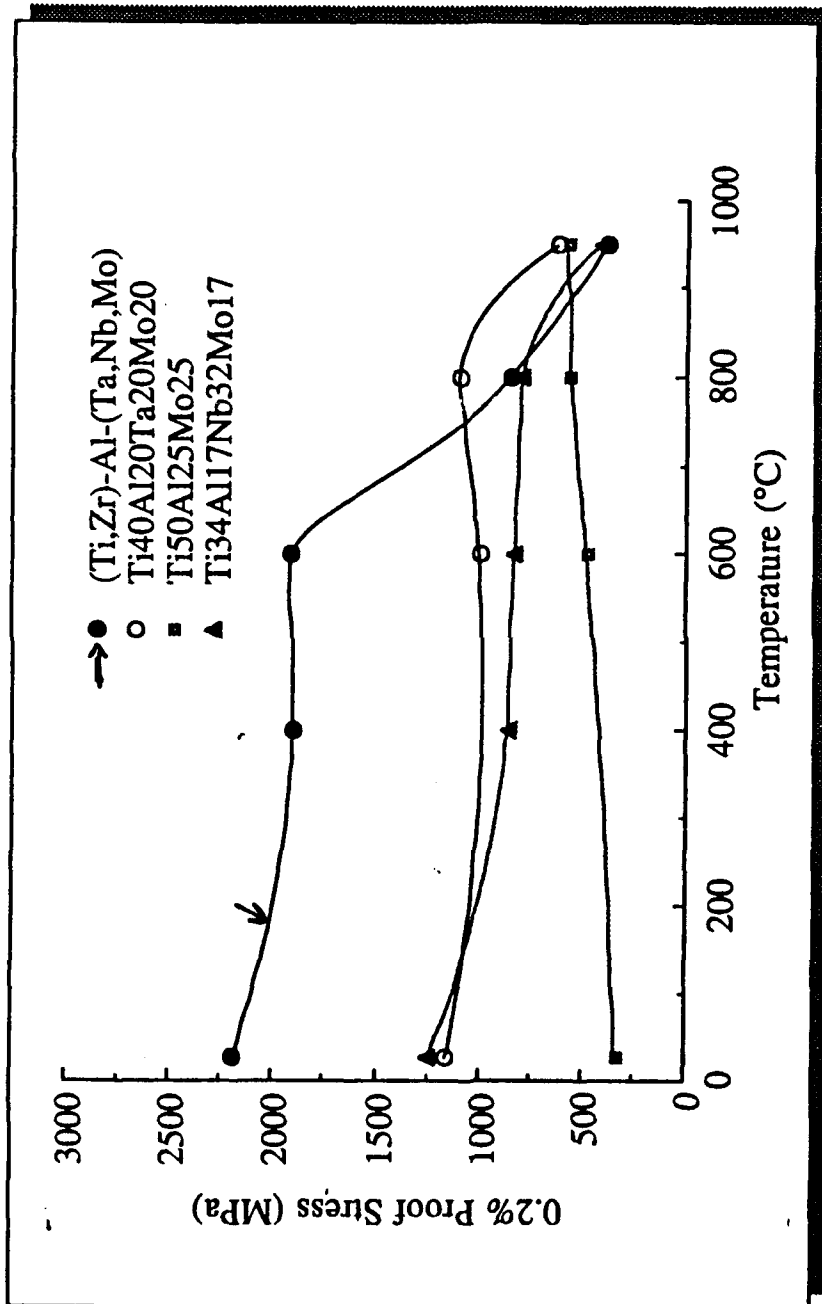
- A2 matrix containing a high volume fraction of second
"compatible" phase
"compatible" : crystal structure and lattice parameter
- Solid state decomposition of solid solution
into two phases
- Empirical "Crystallo-chemical approach
evaluate both size effect and chemical interaction



Two-phase (A2+L₂₁) microstructure
observed in Fe-Ni₂AlTi system



**Two-phase (B2+A2) microstructure observed
in a Ta-base alloy (Ta-Ti-Zr-Al-Nb-Mo system)**

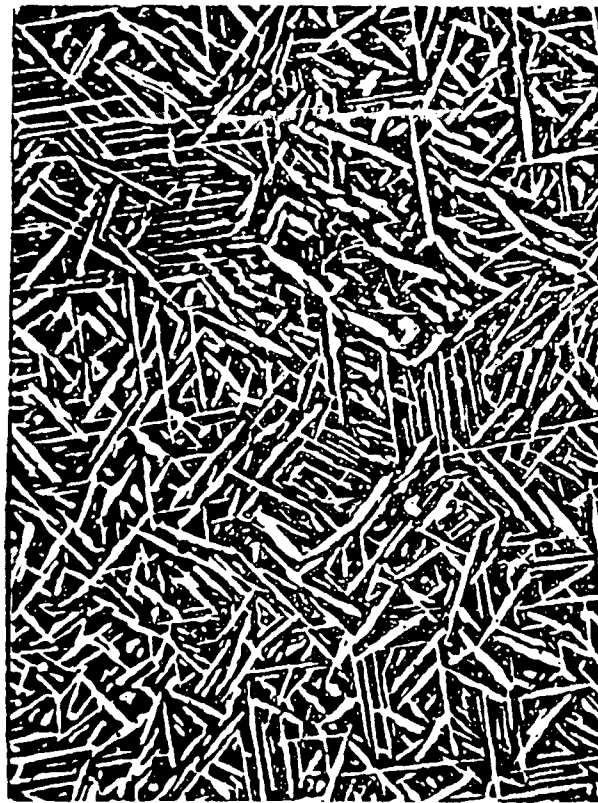


Temperature dependence of yield stress for various alloys :
 Comparison made between a two-phase B₂' + A₂ alloy and
 three single-phase B₂ alloys

NiAl base

Travaux ONERA

ductilité



20 μ m



durcissement



100nm



**4. Microstructure, Processing and Properties
of MoSi₂
D.A. Hardwick
Rockwell Science Centre, USA**

Microstructure, Processing and Properties of MoSi₂

**D. A. Hardwick
Rockwell International Science Center**

work supported by AFOSR



SUMMARY

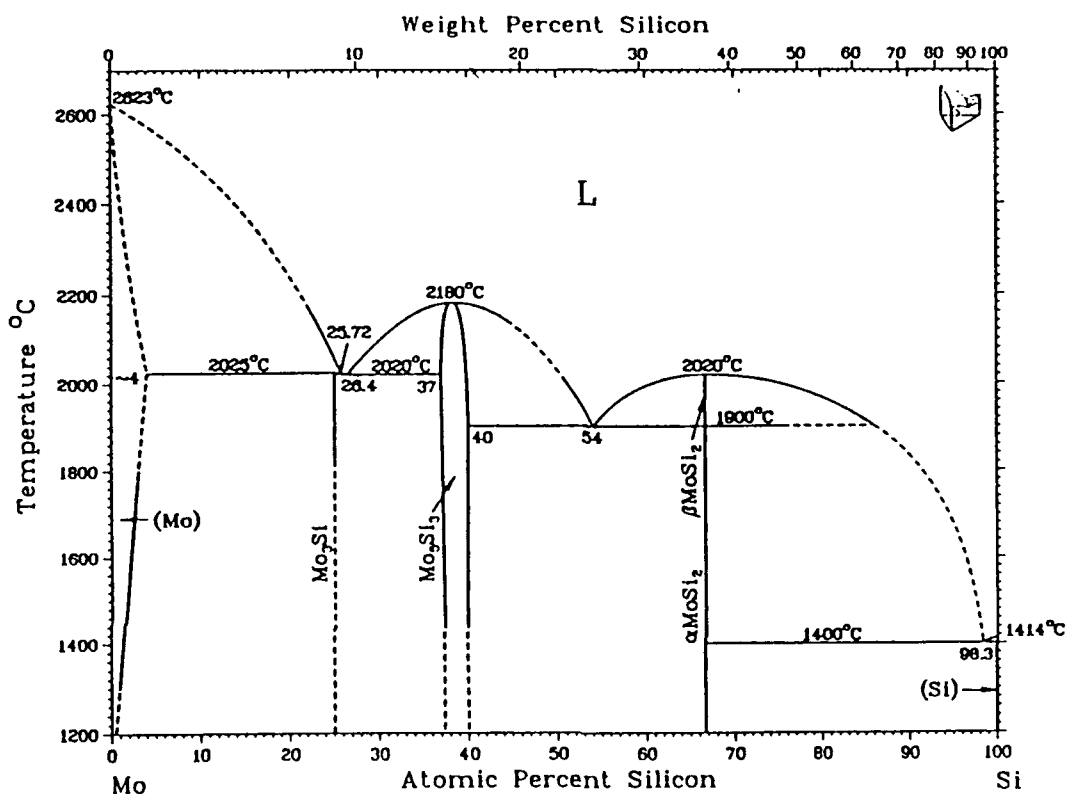
Introduction	:	Historical Background Crystal Structure, Dislocations DBTT, Oxidation Silica as Impurity
RISC Work	:	Our AFOSR program Processing, Microstructure, Properties Comments on Future Directions
Composites	:	Bright Phase Ductile Phase Laminates Composite Design

Background of MoSi₂ Development

- **Early NACA reports, R. A. Long and W. A. Maxwell; 1950 - 1952**
Hot pressed PM material; <100% dense
Oxygen, carbon and grain size effects quantified
Hot tensile, hot compression, tensile creep and oxidation
measured to at least 1300°C
Thermal shock resistance (under stress) of turbine blade
shapes
- **German work began in early 50's as well; Fitzer and students**
which has continued to the present time
Ductile phase (wire) composites with Ta and Nb
- **Soviet reports beginning in mid 50's; Samsonov and**
coworkers on transition element silicides
Thermophysical properties
- **SiC whisker composites work began in mid 80's in US; Carter,**
Gibbs, Petrovic (LANL)
Strength and toughness benefits

Los Alamos

Assessed Mo-Si Phase Diagram



Mo-Si Crystal Structure Data

Phase	Composition, at.% Si	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Mo)	0	<i>cI2</i>	<i>Im3m</i>	A2	W
Mo_5Si	25	<i>cP8</i>	<i>Pm3n</i>	A15	Cr_5Si
Mo_3Si	37.5	<i>U38</i>	<i>I4/mcm</i>	$D8_h$	W_3Si_3
αMoSi_2	66.7	<i>U6</i>	<i>I4/mmm</i>	$C11_b$	MoSi_2
βMoSi_2	66.7	...	$C6_2$	...	...
(Si)	100	<i>cF8</i>	<i>Fd3m</i>	A4	C (diamond)

Dislocations in MoSi₂

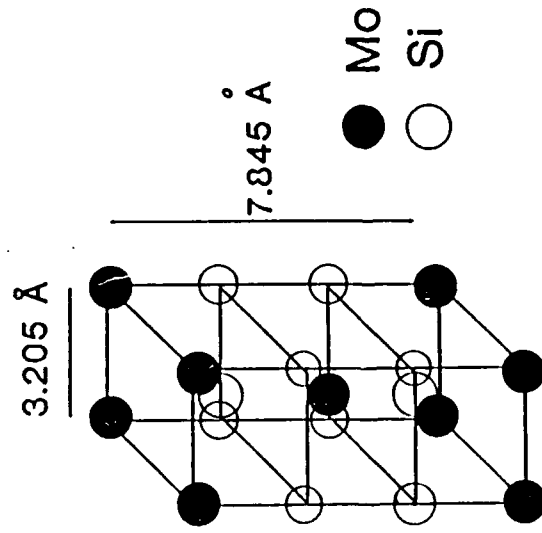
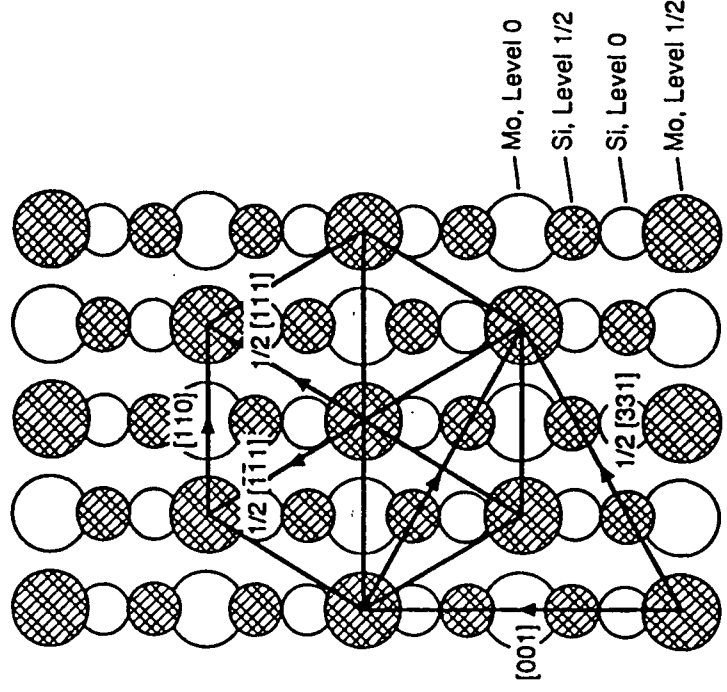
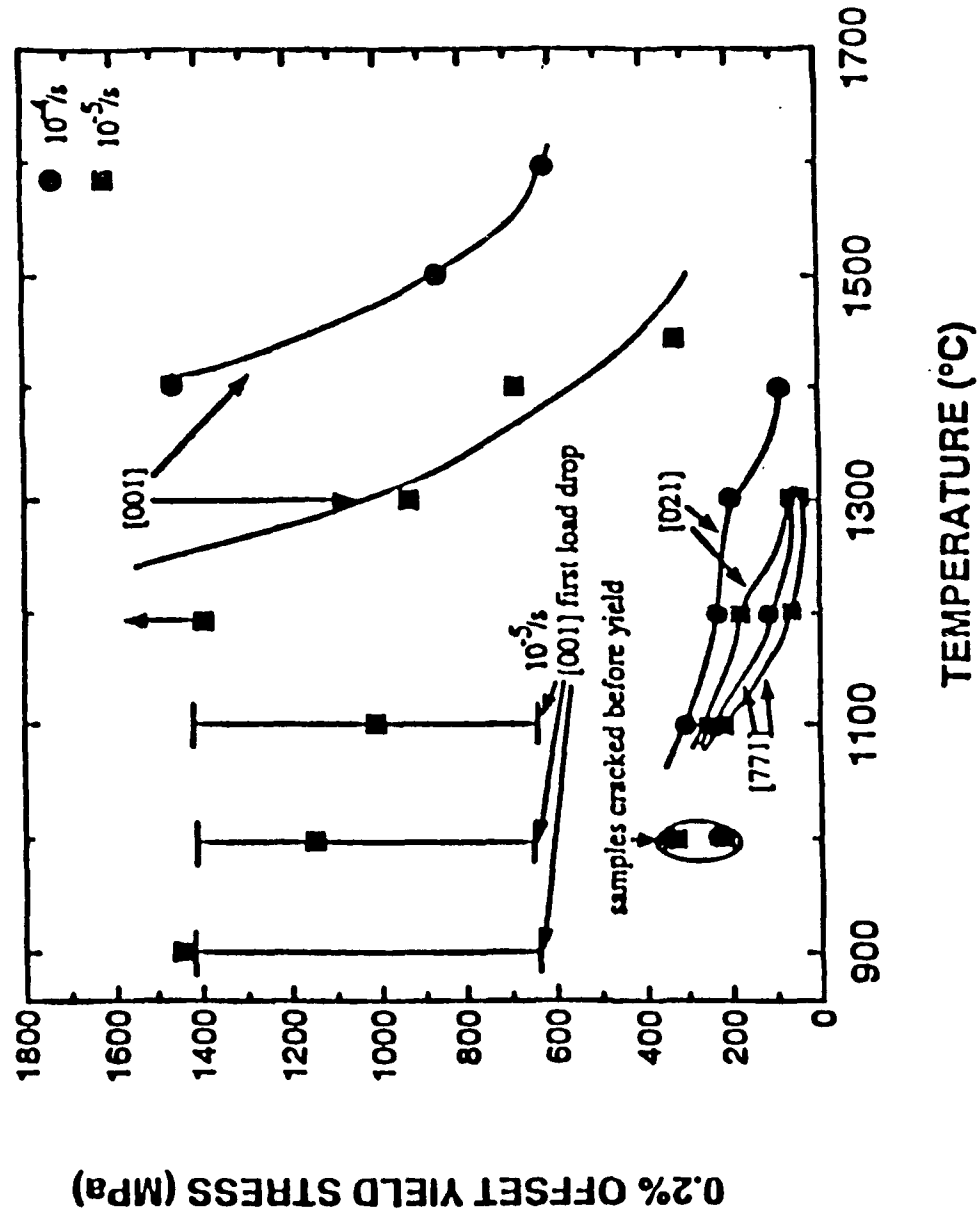


TABLE 1. Possible Burger's vectors and slip planes for MoSi₂

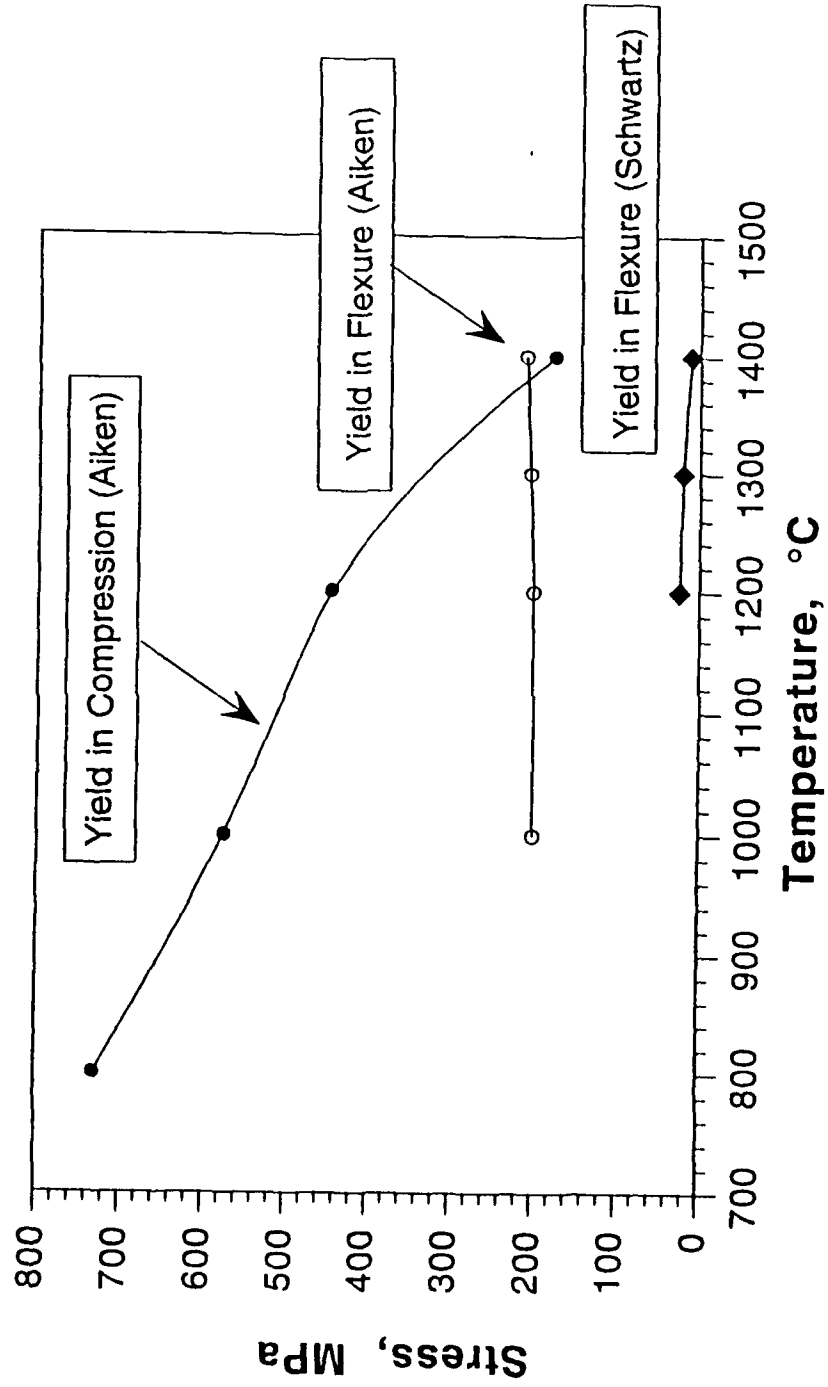
b	Slip planes	b (Å)	$ b ^2$ (Å ²)
✓ $\langle 100 \rangle$	$\{0kl\}$ $011, 001$	3.21 •	10.24
✓ $\langle 110 \rangle$	$\{110\}, \{111\}$	4.54	20.61
✓ $\langle 1/2 \rangle \{111\}$	✓ $\{101\}, \{110\}$	4.53 •	20.56
$[001]$	$\{100\}, \{110\}$	7.85	61.62
$\langle 1/2 \rangle [001]$	$\{110\}, \{013\}$	2.62	6.84
✓ $\langle 1/2 \rangle \langle 331 \rangle$	✓ $\{110\}, \{013\}$	7.86	61.78
$\langle 1/6 \rangle \langle 331 \rangle$	$\{110\}, \{013\}$	2.61	6.82



Compression of Single Crystals



Ductile to Brittle Transition Temperature



Accelerated Oxidation of MoSi₂

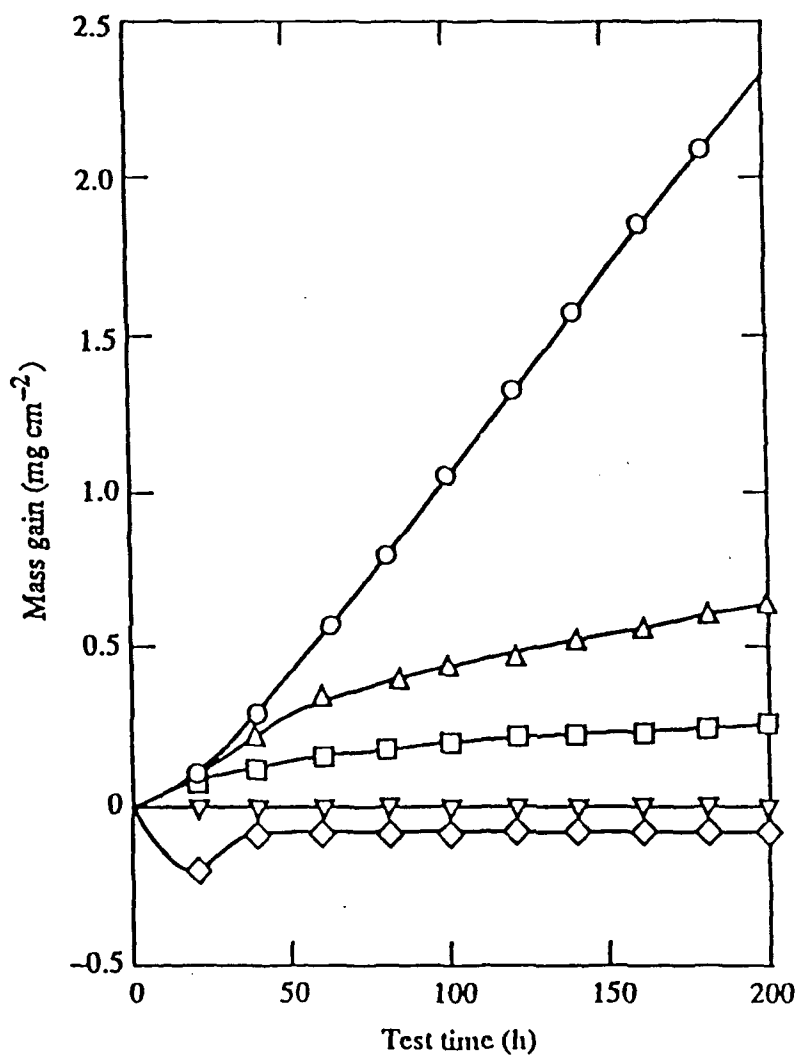
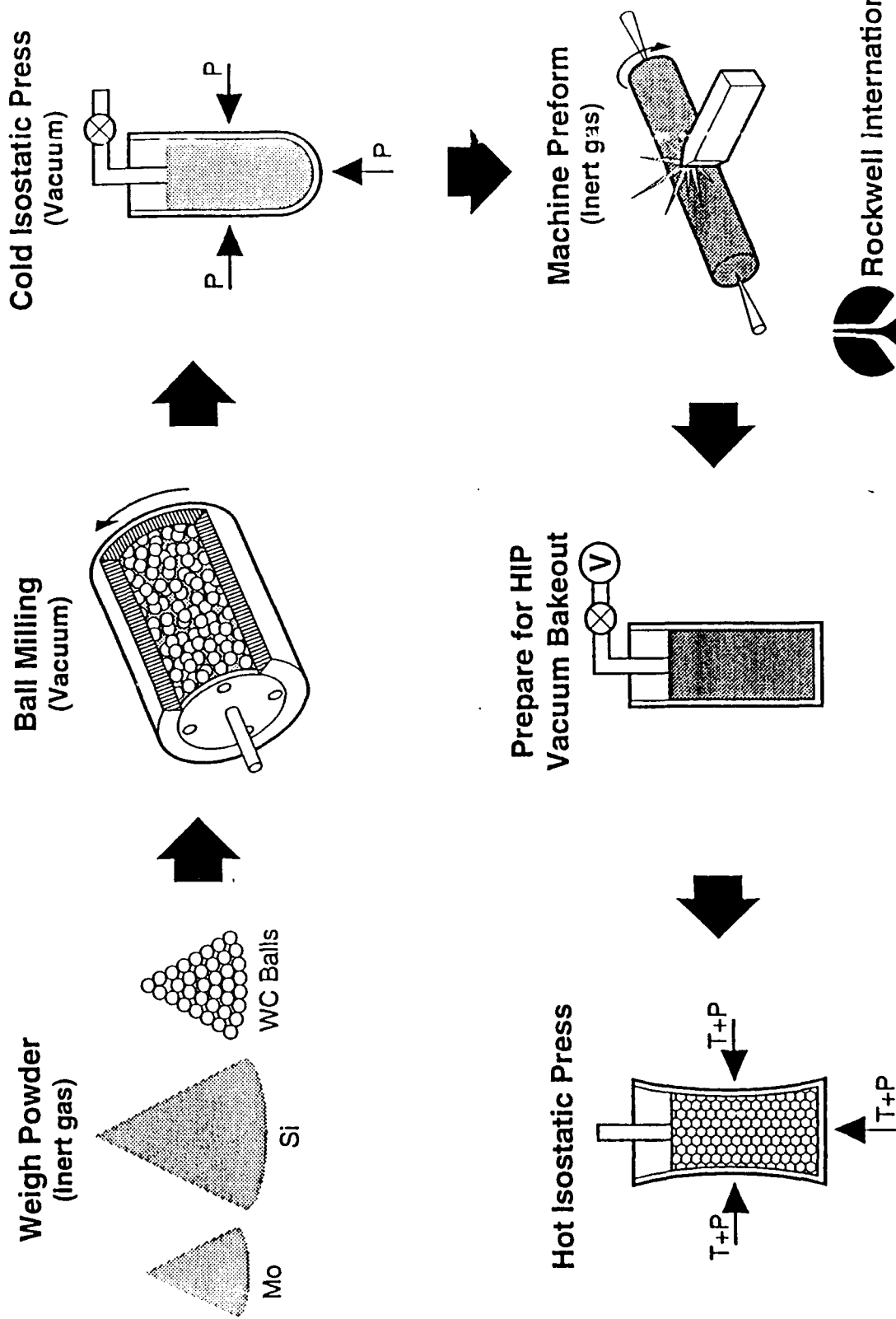


Fig. 2—Cyclic oxidation of CERAC MoSi₂ samples in dry air as a function of temperature: (□) 400 °C; (Δ) 450 °C; (○) 500 °C; (◇) 550 °C; and (▽) 600 °C.

Schematic of Reactive HIP Process

SC-0575-C

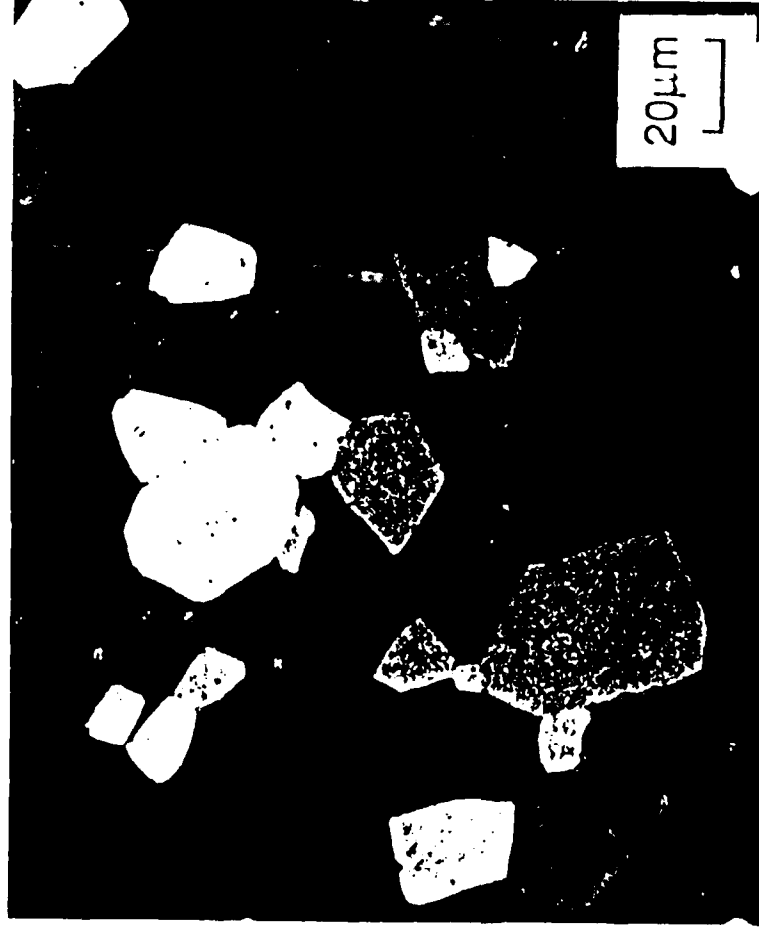


Characteristics of Our Processing Route

- Begins with high purity elemental powder, not commercial silicide powder
- All processing steps in inert environment $\Rightarrow$ clean but tedious
- Produces a 98% dense material with large grain size and low silica content
- Densification assisted by adiabatic heating - low external heat input
- Probably not a feasible process for large scale production



Microstructure of MoSi_2 ; as processed



Optical - polarized light



Rockwell International
Science Center

4.11

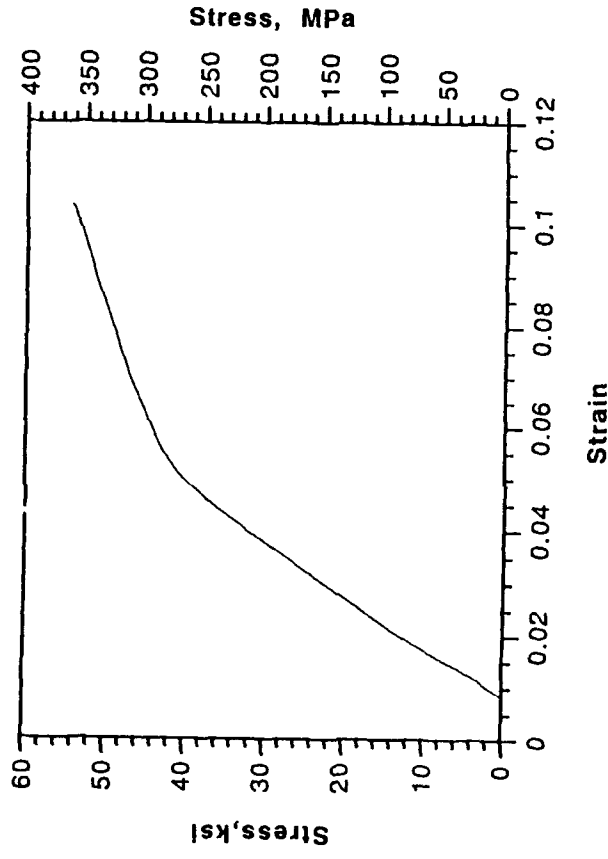
Experimental Parameters

- Compression of right circular cylinders
Simple specimen geometry, simple stress state (cf. bending)
- Temperature range: 1200°C - 1400°C (likely range for DBTT)
- Strain rate range: 10^{-3} sec^{-1} to 10^{-5} sec^{-1}
- Strain range: 1% to 50% (average strain $\approx 10\%$)
- Flow stress, influence of stress on microstructure, deformation mechanisms



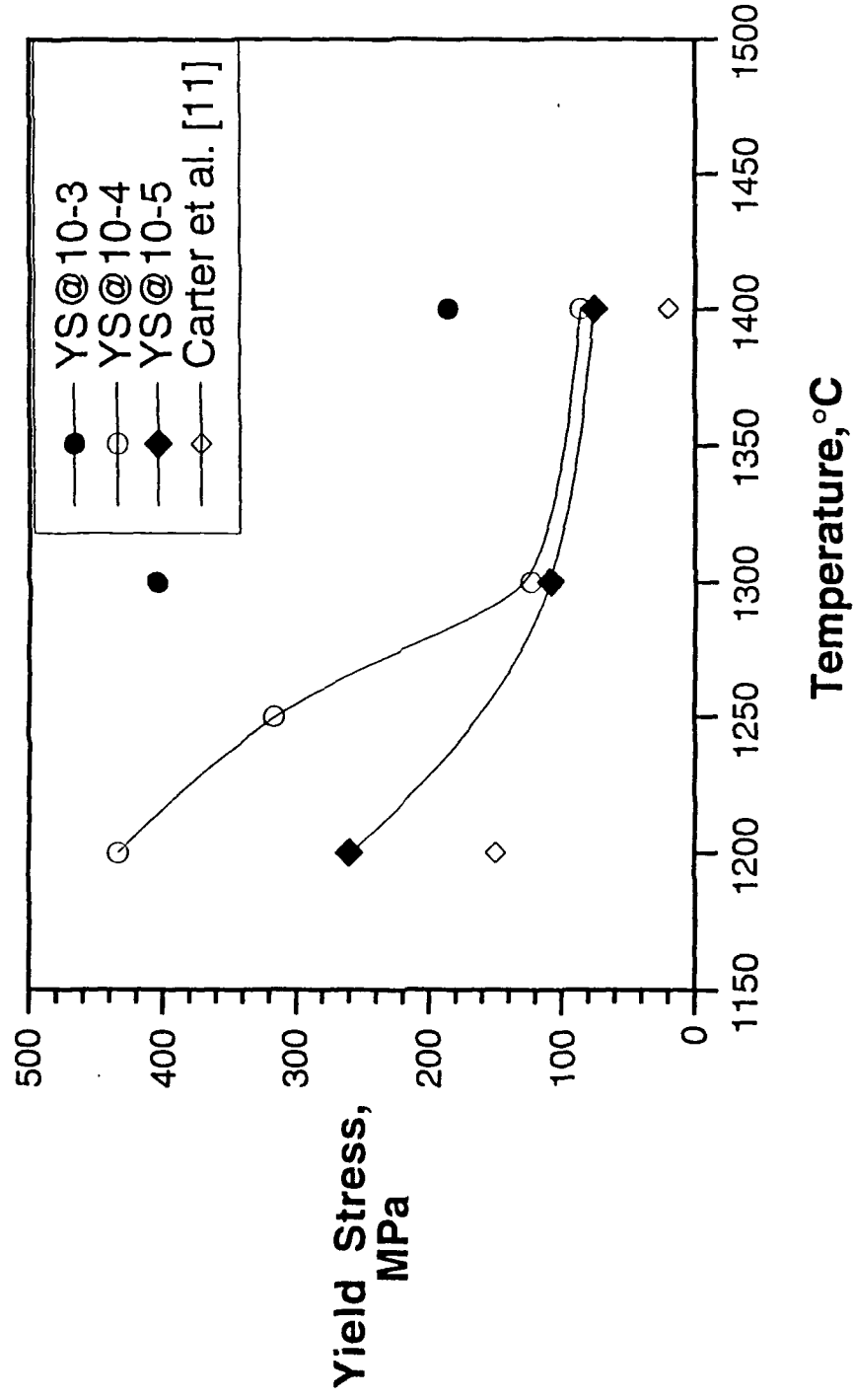
Rockwell International
Science Center

Effect of Microstructure on Mechanical Properties

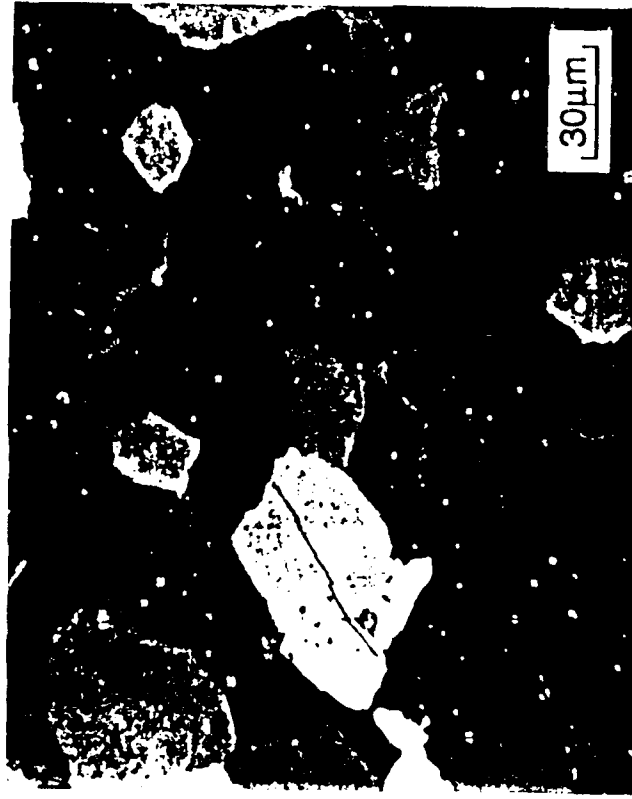


Stress-Strain Curve for Sample Tested at 1200°C and 10^{-5} /sec
Non-linearity in Stress-Strain Curve $\equiv$ Plastic Deformation ?

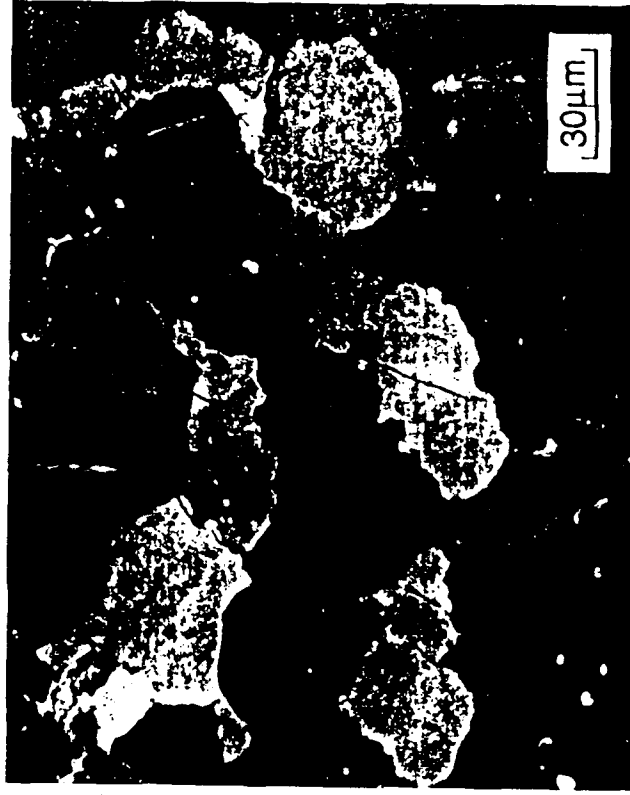
Yield Stress vs Temperature and Strain Rate



Microstructure of MoSi_2 deformed at 10^{-4}sec^{-1}



1250°C; $\epsilon_t = 0.087$



1300°C; $\epsilon_t = 0.15$

Microstructure of MoSi_2 deformed at 10^{-4}sec^{-1}



$1250^\circ\text{C}; \epsilon_t = 0.087$



$1300^\circ\text{C}; \epsilon_t = 0.15$

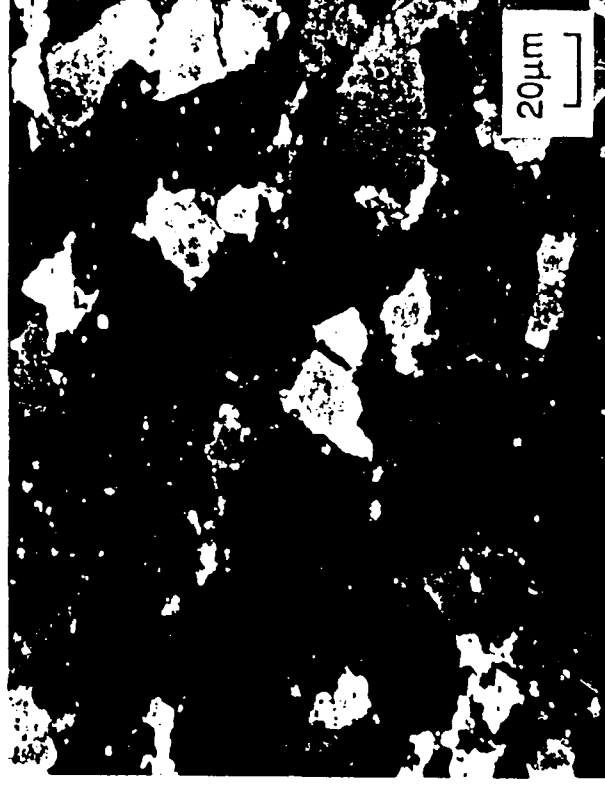
Large Strain Deformation of MoSi_2



1 cm

1 cm

$\epsilon = 0.5 / T = 1300^\circ / \dot{\epsilon} = 1 \times 10^{-5} \text{sec}^{-1}$



20 μm

Optical - polarized light

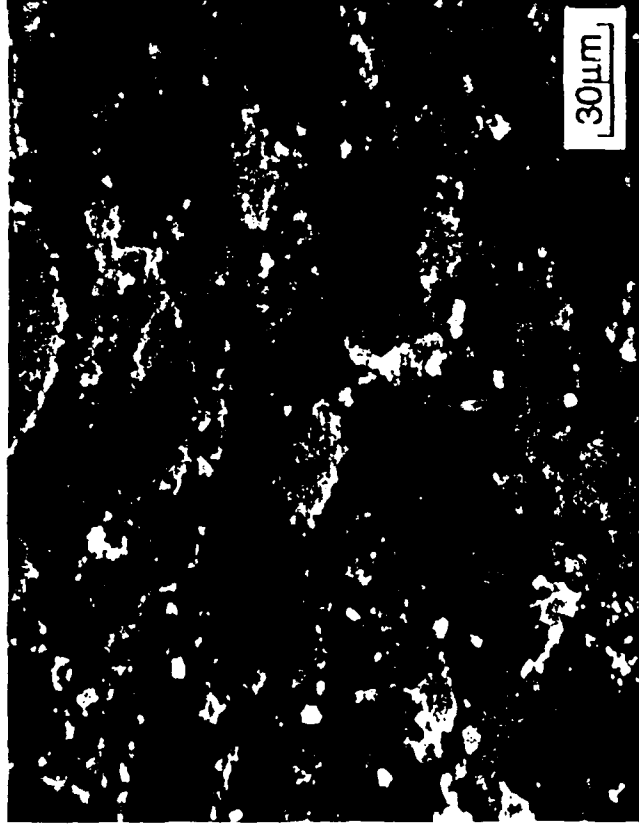


Rockwell International

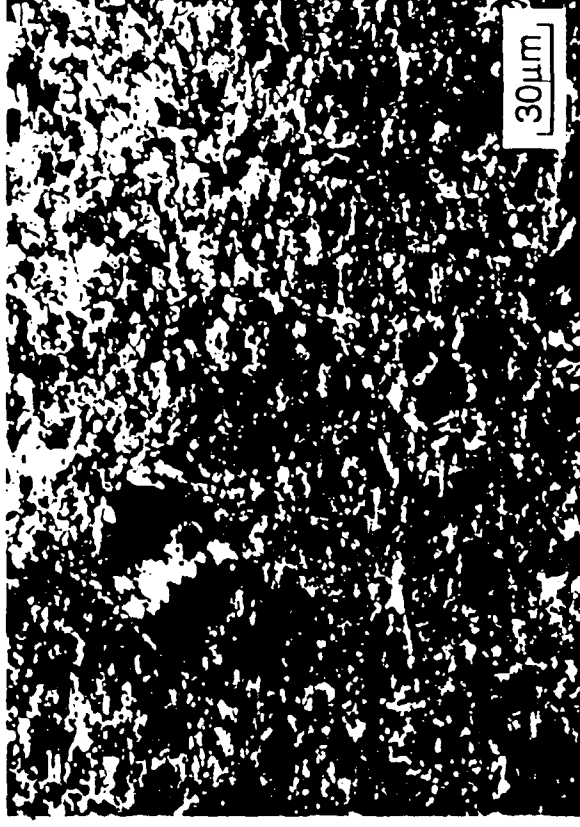
Science Center

4.17

**Microstructure of MoSi_2 ; $e_t = 0.57$
at 1300°C and 10^{-4}sec^{-1}**



Optical - polarized light



SEM - backscatter contrast



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Science Center

Dislocations in MoSi_2 strained at 10^{-4}sec^{-1}



$\epsilon_t = 0.16$; $T = 1300^\circ\text{C}$



$\epsilon_t = 0.14$; $T = 1400^\circ\text{C}$

Implications for Future Work

- Reduce CRSS of hardest orientations by alloying - must be done in single crystals
- Alloying to promote additional slip systems - altering the crystal structure
- Directional solidification to enhance “soft” orientations
- Additions of benign second phase to reduce grain size - decrease slip length so that initial cracks are not catastrophic

Additions of C or rare earths would have combined effect of producing second phase while scavenging oxygen

- Silica should be avoided - it does promote a fine grain size but, in high concentrations, enhances grain boundary sliding. This is one way to avoid microcracking but not the best way!



MoSi₂ Composite Approaches

- Brittle Whiskers or Rods: Increase in creep strength and toughness (via pull-out)
- Hard Dispersoids: Increase in flow stress and work hardening rate
- Ductile Phases (Particulates, Whiskers, Wires): Increase in low temperature toughness (via energy absorption) -- implied creep detriment (?)
- Laminates: Can dramatically affect both strength and toughness depending on the details of the interfacial properties

4.21

Strength and Toughness of MoSi₂ Composites

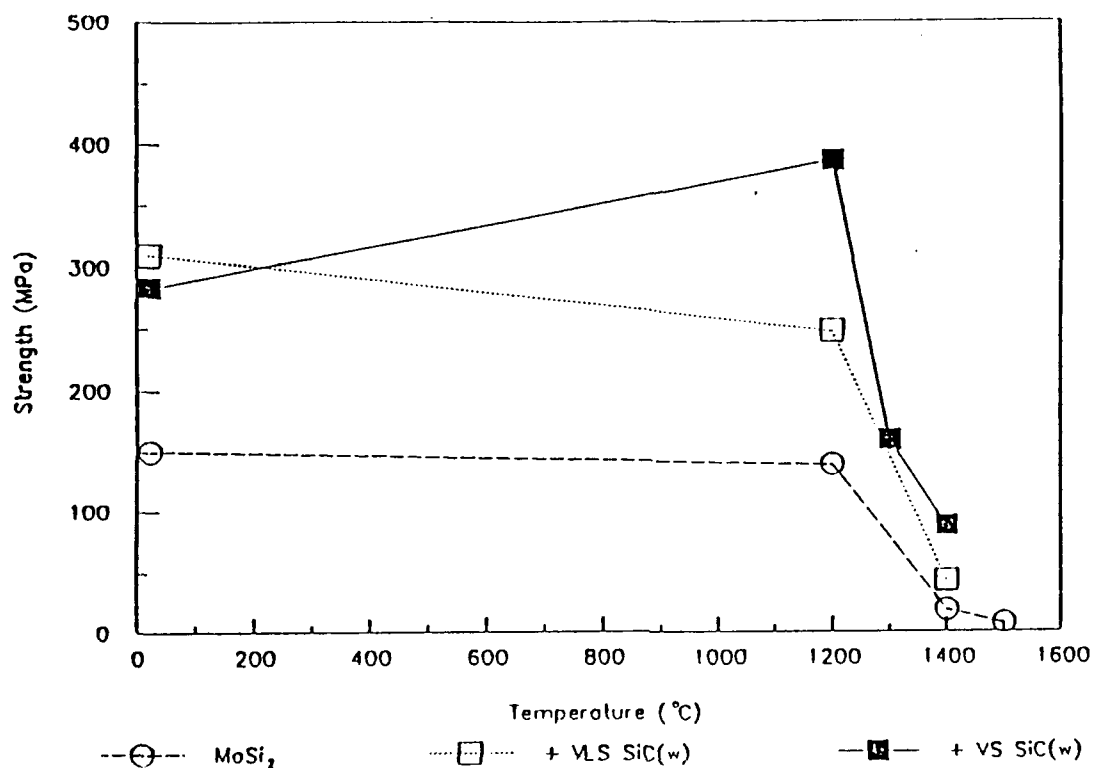
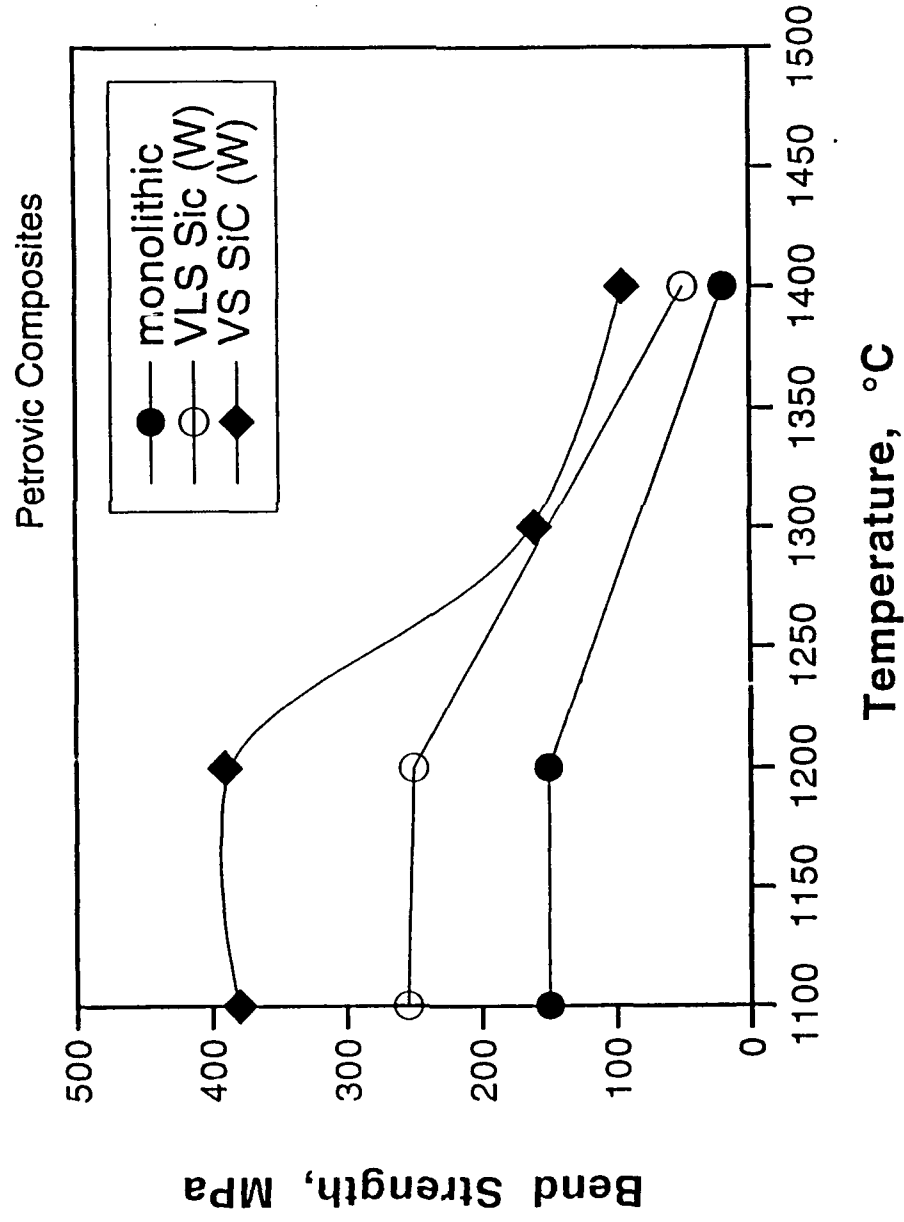


Table 1: Room Temperature Fracture Toughness Data

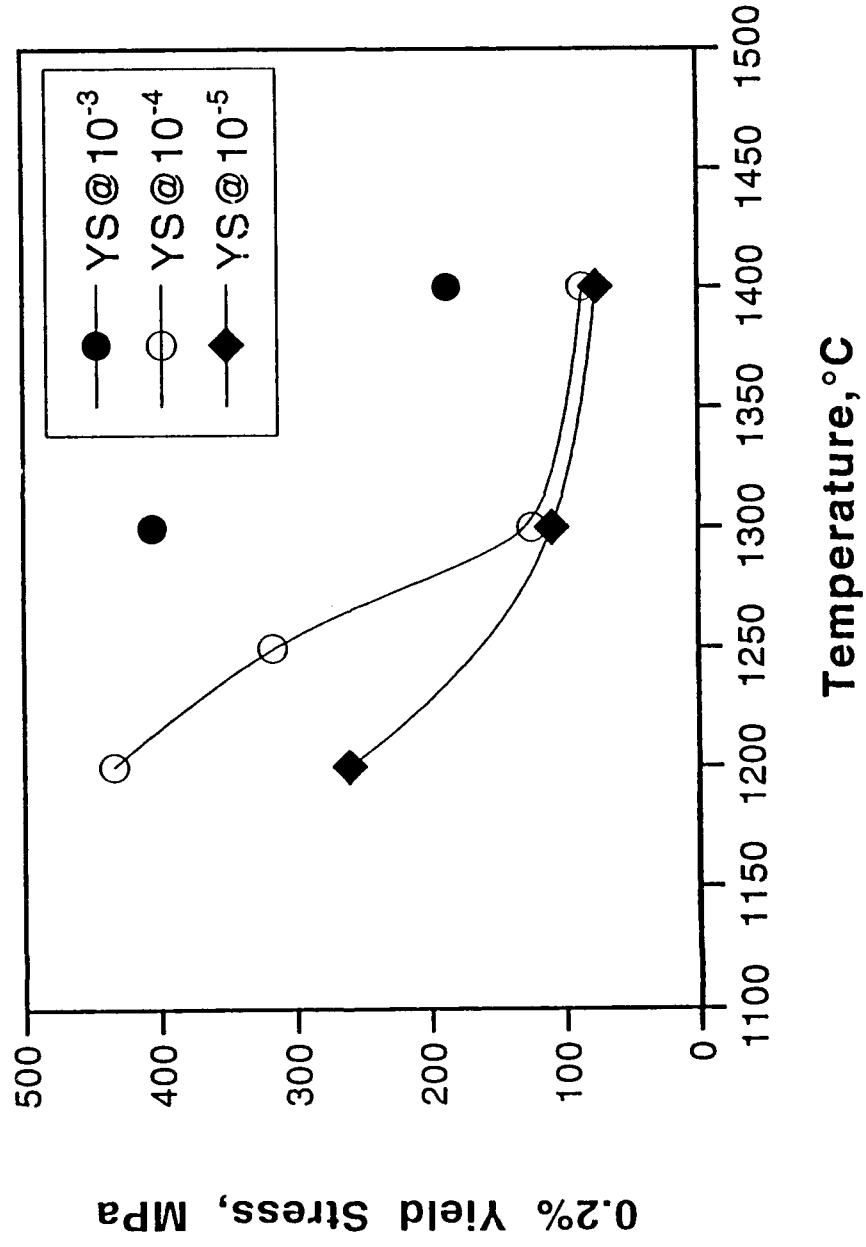
	MoSi ₂	MoSi ₂ + VLS SiC(w)	MoSi ₂ + VS SiC(w)
MPa·m ^{1/2} (ksi·in ^{1/2})	5.32 (4.84)	8.20 (7.45)	6.59 (5.99)

From: D. H. Carter, J. J. Petrovic, R. E. Honnell and W.Scott Gibbs, "SiC - MoSi₂ Composites", Los Alamos National Laboratory, LA-11577-MS, June 1989.

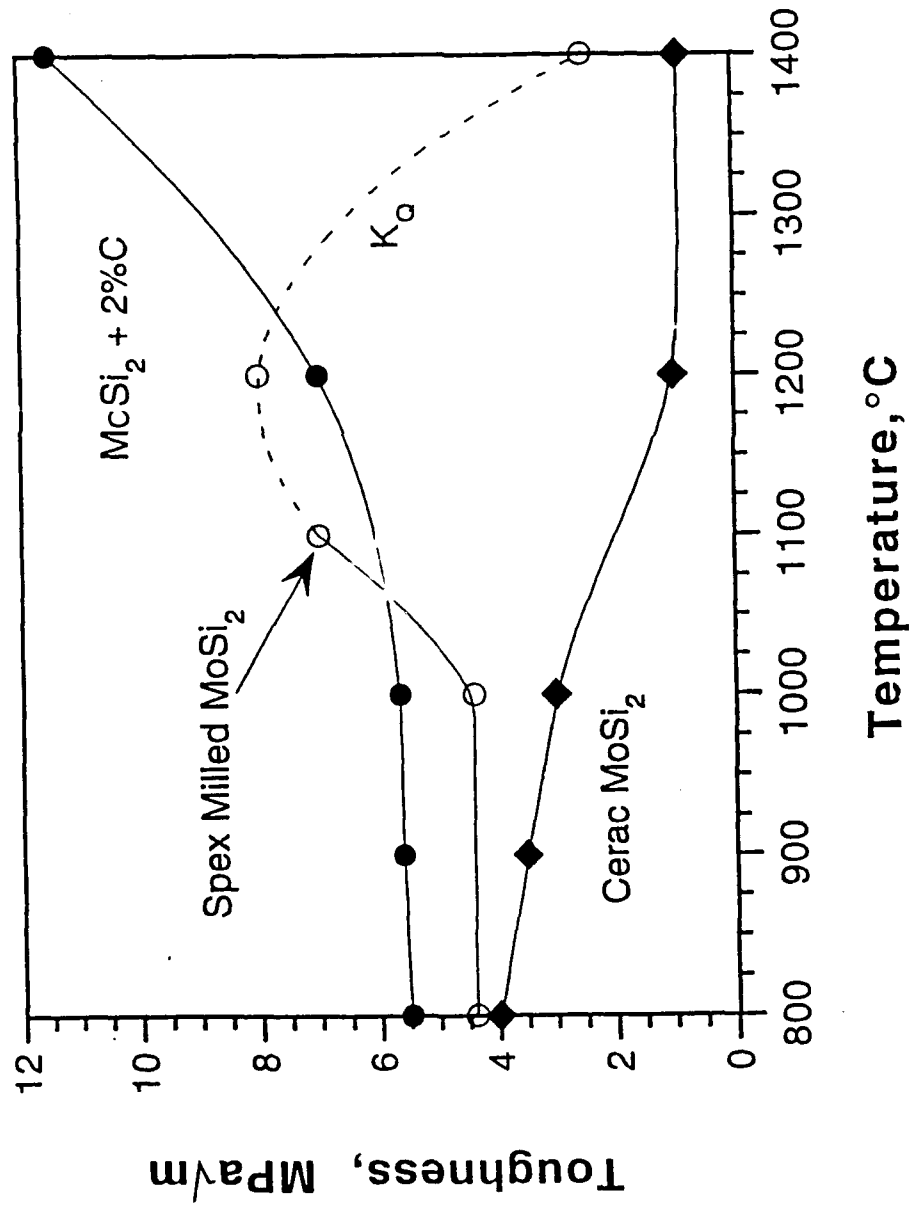
Strength of Molybdenum Disilicide



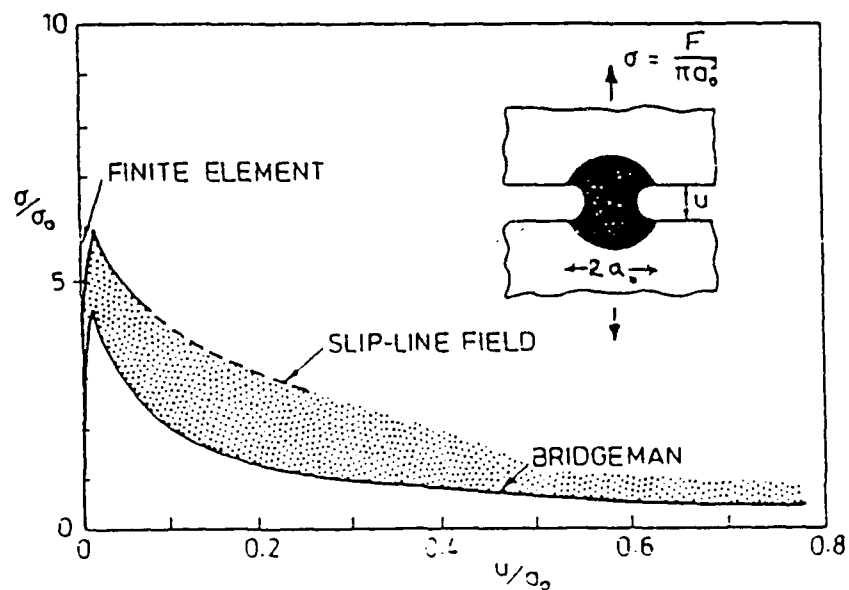
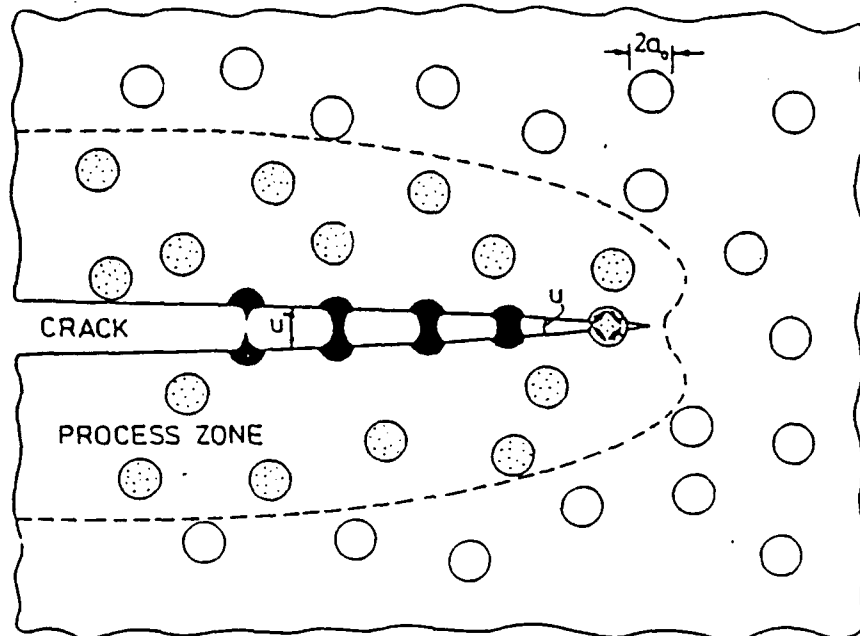
Strength of Molybdenum Disilicide



Toughness of Molybdenum Disilicide



Ductile Phase Toughening by Crack Bridging (Evans, Ashby, McMeeking, Mehrabian et al)

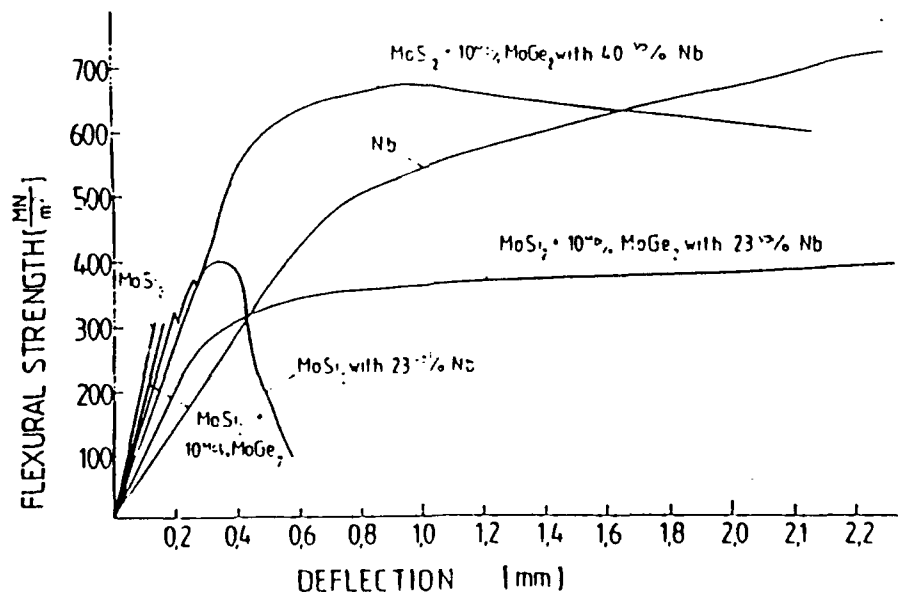


Issues Concerning Ductile Phase Toughening

- Thermodynamic compatibility with MoSi_2 matrix
- High temperature strength decrement due to 'soft' refractory metal additions
- Effect of metal additions on physical properties; density, modulus, thermal expansion, oxidation etc.

Nb Wire Reinforced MoSi₂

- Hot pressed; $\approx 95\%$ dense; 5 mm dia. wires; 50 vol%;
reaction zone $\approx 10\mu\text{m}$
- Impact resistance increased 700% vs. unreinforced MoSi₂
- High Temperature Bend Strength*:
500 MPa @ 1200°C
200 MPa @ 1300°C
- Room Temperature Bend Strength**:



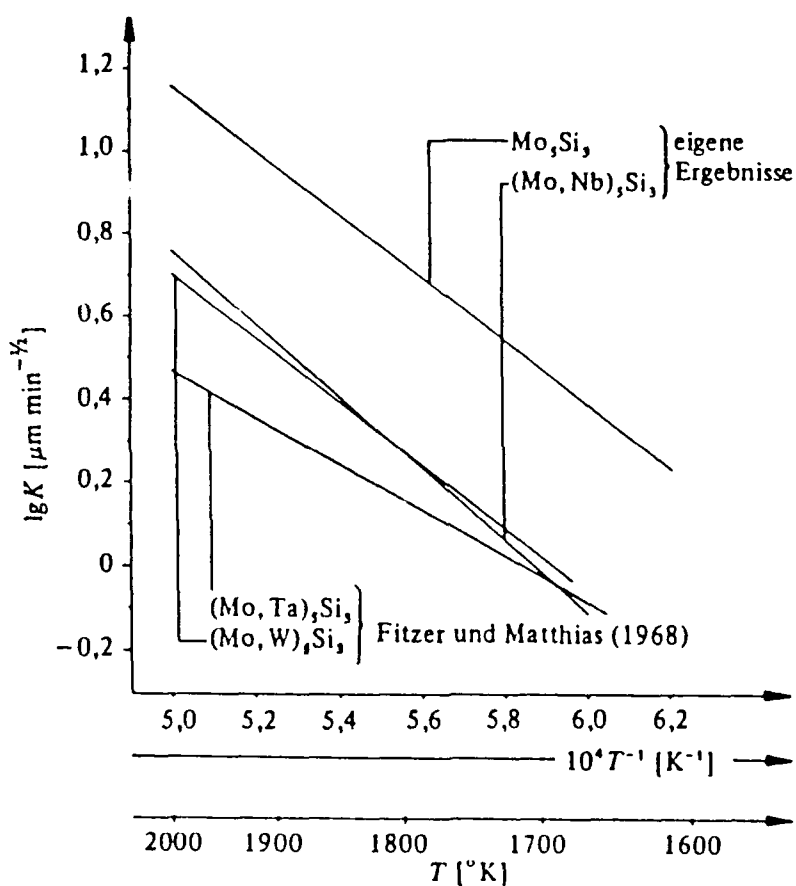
* Ref.: J. Schlichting, *High Temp. - High Pressures*, 10, (1978), 241.

** Ref.: E. Fitzer and W. Remmele, Fifth International Conf. on Composite Materials ICCM-V, (1985), 515.



Rockwell International

Parabolic Rate Constant for Growth of M_5Si_3 in Contact with $MoSi_2$



Ref.: E. Fitzer and F. K. Schmidt, *High Temp. - High Pressures*, 3, (1971) 445.

Toughness of Laminated Composites

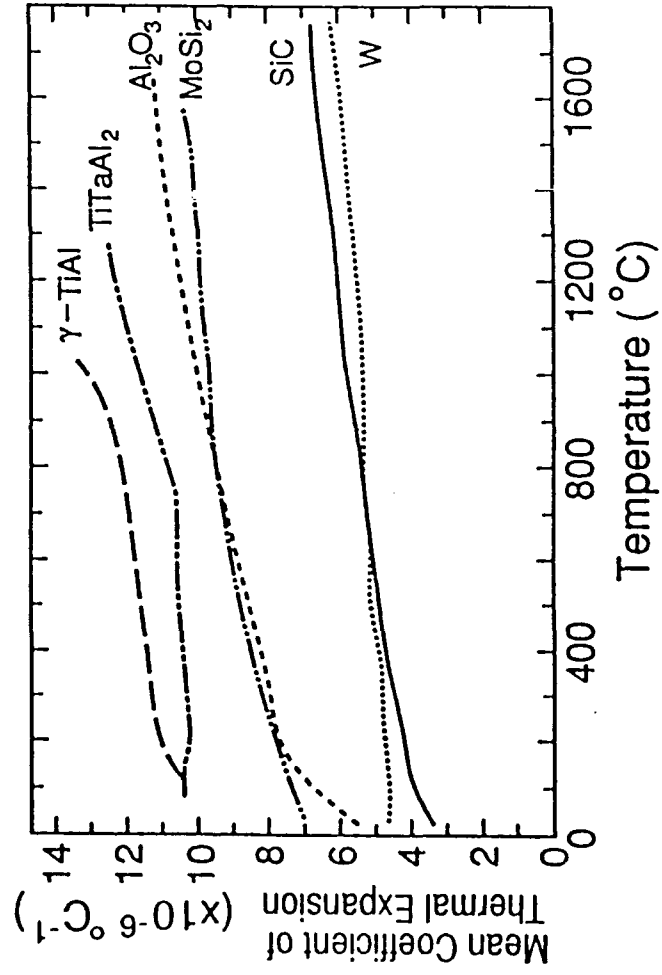
Table III. Measured Toughness of the Laminated Composites Reinforced with 20 Vol Pct of Nb Foils with a Thickness of 0.25 mm*

Material	Monolithic MoSi ₂	Uncoated Nb Reinforced	Al ₂ O ₃ Coated Nb Reinforced	ZrO ₂ Coated Nb Reinforced	ZrO ₂ Coated Nb Reinforced
Hot-pressing temperature	1700 °C	1700 °C and 1400 °C	1400 °C	1400 °C	1700 °C
Damage tolerance (MPa · m ^{1/2})	3.3 ± 0.3	15.2 ± 1.3	14.0 ± 1.5	12.8 ± 1.5	8.6 ± 1.3
Work of fracture (J/m ²)	690 ± 30	21,600 ± 3000	28,700 ± 1900	28,700 ± 4600	2800 ± 300
Interfacial fracture energy**	—	high	medium	low	low
Ductility of the reinforcement**	—	high	high	high	low

*Four specimens for each condition were tested except for Al₂O₃ coated Nb system for which eight specimens were tested.

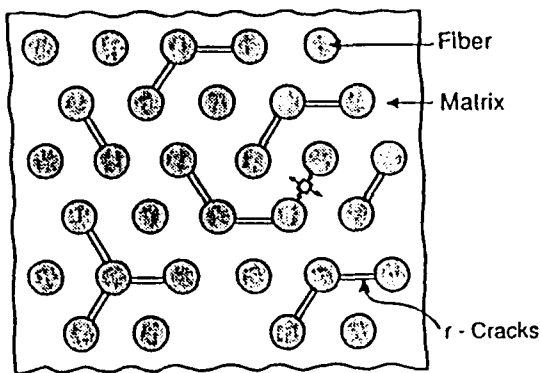
**For details, see Tables I and II.

Thermal Expansion Coefficients

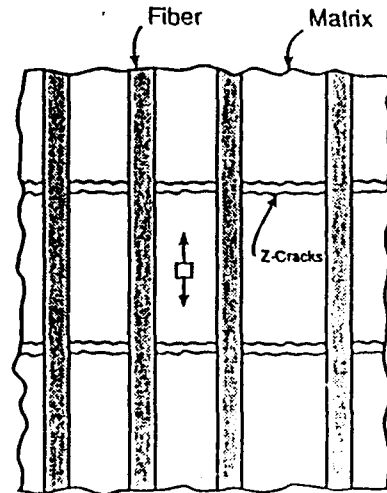


CTE Cracking in Brittle Matrix Composites

radial r-cracks



normal z-cracks



$$\mathcal{R} = R(E_m \epsilon_T / K_m)^2$$

R = reinforcement size

K_m = matrix toughness

E_m = matrix modulus

ϵ_T = misfit strain = $f(\Delta\alpha)$

$\mathcal{R}_c$ = critical size below which no cracking occurs

CTE-induced Matrix Cracking

R_C depends on

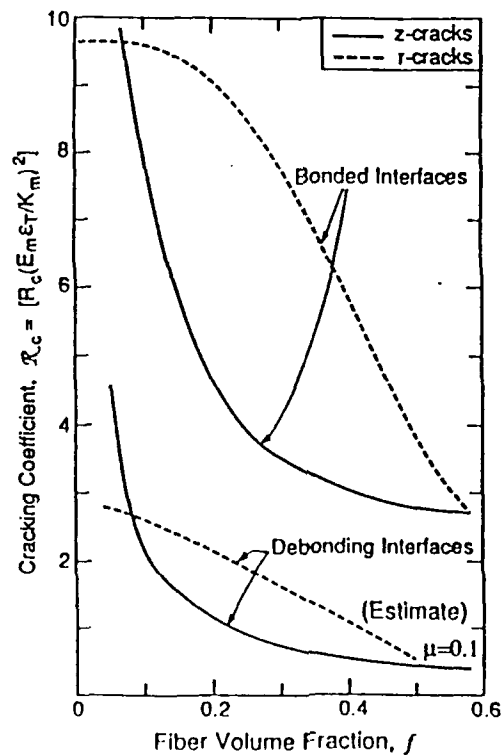
f = volume fraction of reinforcement

Σ = ratio of elastic moduli

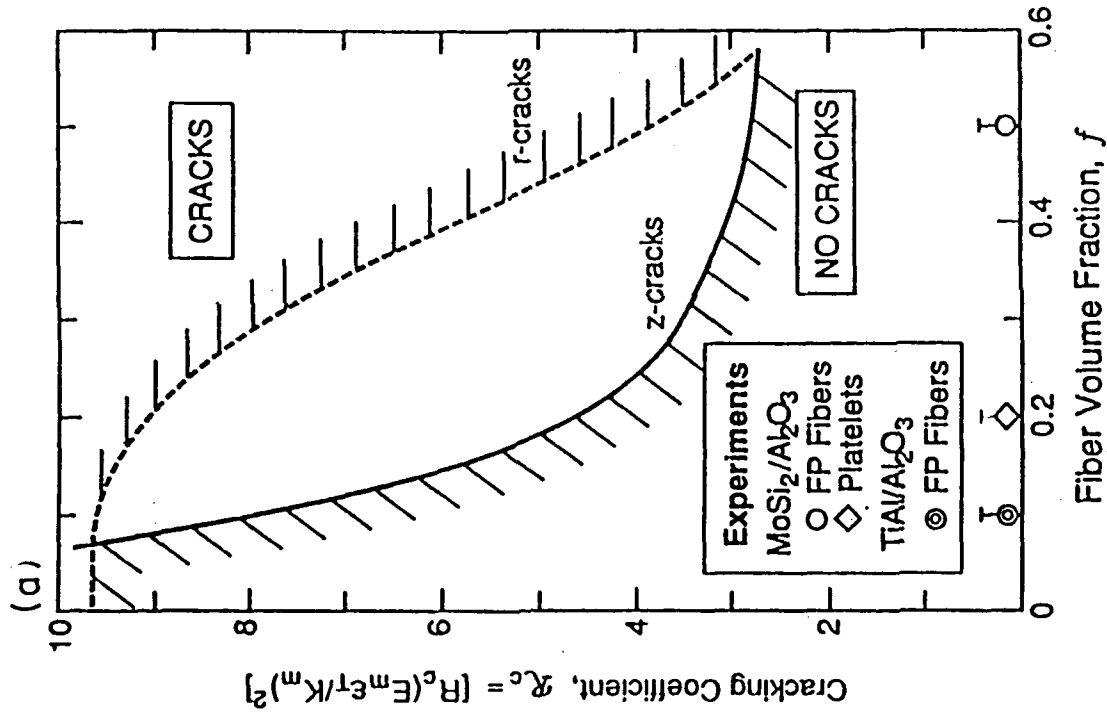
ν = Poisson's ratio

μ = interface response (friction coefficient)

Trends in cracking coefficient with volume fraction

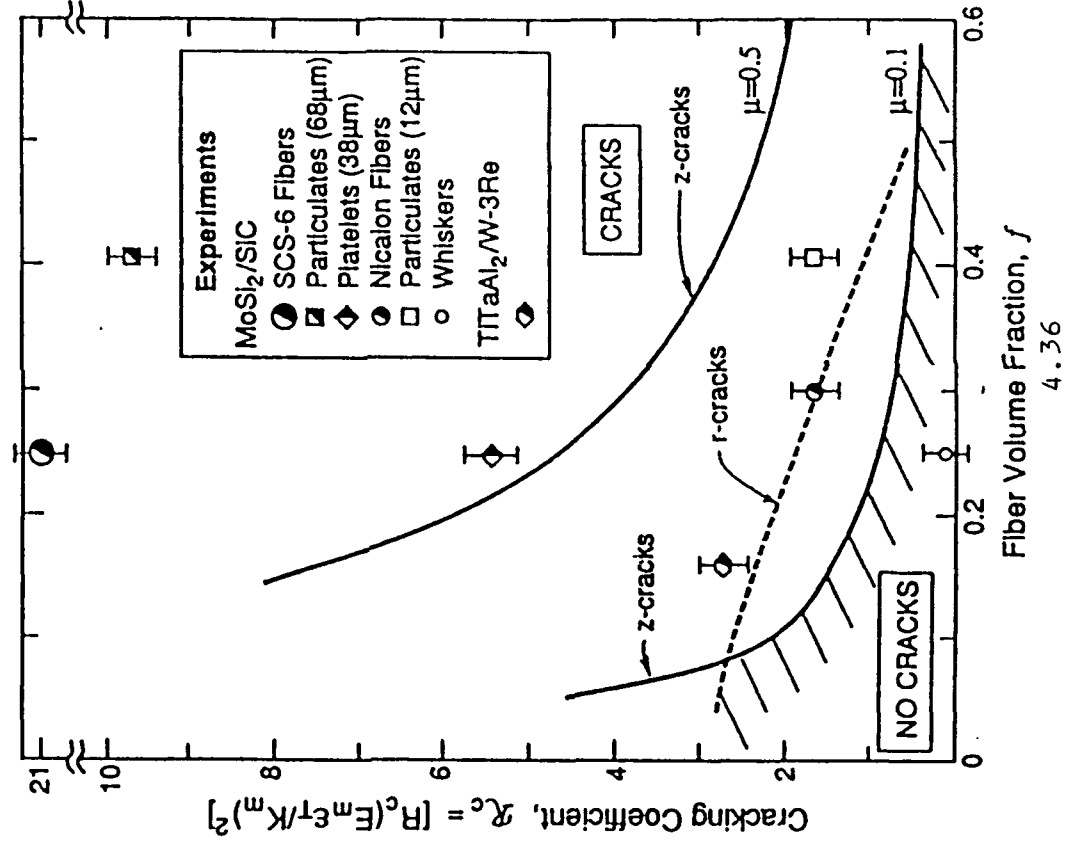


MoSi₂ reinforced with Al₂O₃



CTE Matrix Cracking - Debonding Interfaces

MoSi₂ reinforced with SiC



**5. Effect of Microstructure on the Creep of
Molybdenum Disilicides and their Composites
K. Sadananda and R. Feng
Naval Research Laboratory, USA**

EFFECT OF MICROSTRUCTURE ON THE CREEP OF MOLYBDENUM
DISILICIDES AND THEIR COMPOSITES

K. SADANANDA AND C.R. FENG
NAVAL RESEARCH LABORATORY
WASHINGTON D.C.

OUTLINE

1. WHY MOLYBDENUM DISILICIDES?
2. MICROSTRUCTURE: MONOLITHIC MATERIAL VS COMPOSITES
 - (a) PARTICULATES VS WHISKERS
 - (b) DISTRIBUTION OF REINFORCEMENTS AND ASPECT RATIO
 - (c) GRAIN SIZE EFFECTS VS REINFORCEMENT EFFECTS
 - (d) ALLOYING EFFECTS
3. CREEP PROCESS
4. HOW DO THE MOLYDISILICIDES COMPARE WITH OTHER POTENTIAL
CANDIDATE MATERIALS FOR HIGH TEMPERATURE
APPLICATIONS

TABLE - 1

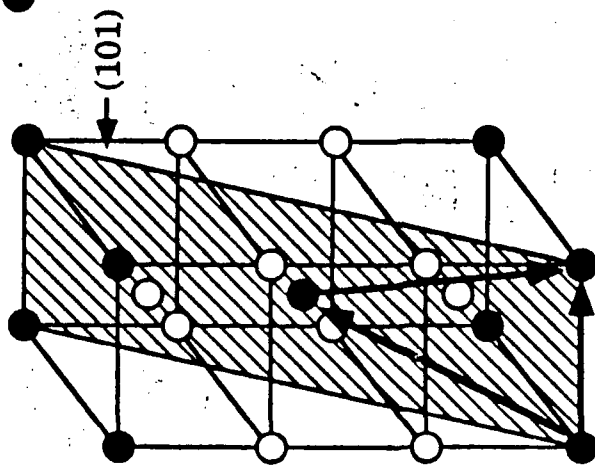
CANDIDATE MATERIALS FOR HIGH & LOW TEMPERATURE APPLICATIONS

<u>< 1000°C</u>		<u>> 1000°C</u>	
Nickel base Superalloys MAR M-246		SI-based Ceramics SiC, Si ₃ N ₄ , SiC/SiC	
• NI-aluminides		• NIAI, NbAl ₃ , TaAl ₃	
• TI-aluminides		• MoSi ₂	
• COMPGLAS			

TABLE. 1 List of candidate materials for high (>1000 °C) and low (<1000 °C) temperature applications.

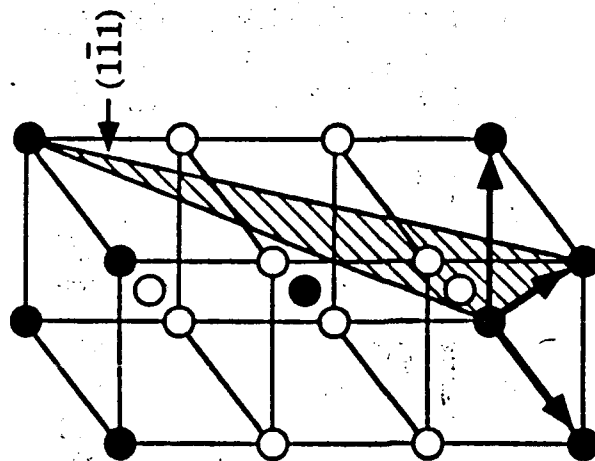
Fig 20

● Mo ○ Si



$$\frac{1}{2} [\bar{1}11] + \frac{1}{2} [11\bar{1}] \rightarrow [010]$$

(a)



$$[100] + [010] \rightarrow [110]$$

(b)

NRL EFFORT ON MOLYBDENUM DISILICIDE COMPOSITES

✓ MONOLITHIC MoSi_2

✓ MoSi_2 + 20% SiC WHISKERS

MoSi_2 + SiC PARTICULATES

10% VOLUME FRACTION

20% VOLUME FRACTION

30% VOLUME FRACTION

✓ 40% VOLUME FRACTION

✓ MONOLITHIC MoSi_2 + WSi_2 ALLOY

✓ MoSi_2 + WSi_2 ALLOY + 20% SiC WHISKERS

MoSi_2 MONOLITHIC - EFFECT OF GRAIN SIZE

MoSi_2 MONOLITHIC + %C (TO ELIMINATE AMORPHOUS SILICA PHASE)

* ALL MATERIALS PROVIDED BY J. PETROVIC OF LOS ALAMOS NATIONAL LABORATORY

Creep Data for MoSi₂

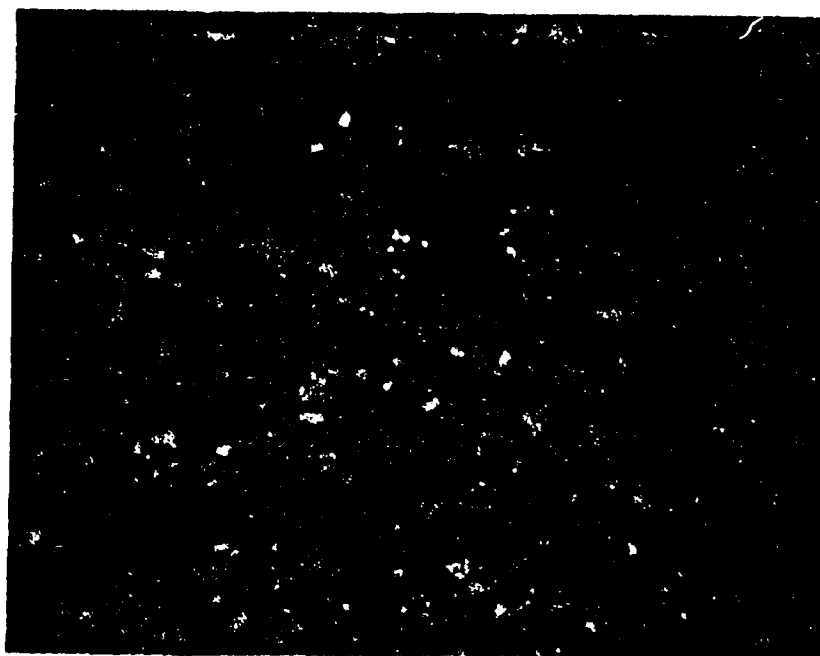
Material	Temp., °C	Stress, MPa	n	Act. Eng., kJ/mol	Ref.
MoSi ₂	1093-1371	8-70	1.3	-	Maxwell
MoSi ₂	1200	42-130	3.5	-	Suzuki et al
MoSi ₂ , HP	1200	35-70	2.8	-	Bose
MoSi ₂ , HIP	1200	35-70	2.8	-	Bose
MoSi ₂	1100-1400	10-80	1.7, 4.4	372	Ghosh et al
MoSi ₂	1100-1300	10-80	2	433	Sadananda et al
MoSi ₂ , single crystal <210>	1200	70-170	2	-	Bose
MoSi ₂ *	1200	10-50	2.7	-	Ghosh et al
(Mo,W)Si ₂ , HP	1200	35-70	1.6	-	Bose
(Mo,W)Si ₂	1100-1400	2-200	2.4-3.6	536	Sadananda et al
MoSi ₂ +20v%SiC _w , HP	1200	35-70	3.1	-	Bose
MoSi ₂ +18v%SiC _w , HIP	1200	35-100	3.1	-	Bose
MoSi ₂ +20v%SiC _w	1200	100-250	3.1	-	Ghosh et al
MoSi ₂ +20v%SiC _w	1100-1450	20-200	3.3, 5.2	596	Sadananda et al
(Mo,W)Si ₂ +20v%SiC _w	1100-1400	8-250	2, 4	-	Sadananda et al
(Mo,W)Si ₂ +20v%SiC _w *	1175	30-50	3.2	557	Wiederhorn et al
(Mo,W)Si ₂ +20v%SiC _w *	1225	30-50	2.3	557	Wiederhorn et al
MoSi ₂ +20v%SiC _p , HIP	1200	50-100	2.5	-	Bose
MoSi ₂ +20v%SiC _p +10Nb _p ,HIP	1200	65-120	3.5	-	Bose
MoSi ₂ +20v%SiC _p	1100	40-90	5	-	Deve et al
MoSi ₂ +20v%SiC _p /Mo	1100	70-150	3	-	Deve et al
MoSi ₂ +20v%SiC _p	1200	8-100	3.1	-	Ghosh et al
XD MoSi ₂ +30v%SiC _p	1050-1300	35-300	3.5	430	Suzuki et al
MoSi ₂ +20v%Er ₂ Mo ₃ Si ₄ p	1200-1300	100-280	3.5	-	Patrick et al
MoSi ₂ +20v%CaO _p	1200	100-310	3.5	-	Patrick et al
MoSi ₂ -45v%Mo ₅ Si ₃ ,HP	1200-1300	10-110	2.5, 3.5	-	Mosan et al
MoSi ₂ -45v%Mo ₅ Si ₃ ,DS	1100-1300	150-1000	4.5	300	Mosan et al
MoSi ₂ +5v%SiC _p	1100-1200	20-180	1	460	Sadananda et al
MoSi ₂ +10v%SiC _p	1100-1200	20-250	1	460	Sadananda et al
MoSi ₂ +20v%SiC _p	900-1200	15-450	1, 4	460	Sadananda et al
MoSi ₂ +30v%SiC _p	1100-1200	35-300	3, 5.7	460	Sadananda et al
MoSi ₂ +40v%SiC _p	1000-1200	40-400	5	460	Sadananda et al
MoSi ₂ +5v%SiC _p *	1050-1150	10-30	1	815	Wiederhorn et al
MoSi ₂ +10v%SiC _p *	1050-1150	10-30	3	575	Wiederhorn et al
MoSi ₂ +20v%SiC _p *	1050-1150	10-30	5	894	Wiederhorn et al
MoSi ₂ +30v%SiC _p *	1150-1250	30-50	5	684	Wiederhorn et al
MoSi ₂ +40v%SiC _p *	1100-1200	30-50	5, 10	628	Wiederhorn et al
MoSi ₂ +1wt%C	1200-1400	20-250	2, 5	460	Sadananda et al
MoSi ₂ +2wt%C	1000-1400	20-300	3	460	Sadananda et al
MoSi ₂ +4wt%C	1200-1400	20-250	3	460	Sadananda et al

* Tensile Creep Test



100 MICRONS

50/50 MOLE % $\text{MoSi}_2/\text{WSi}_2$



100 MICRONS

30 VOL. % SiC PARTICLE-50/50 MOLE % $\text{MoSi}_2/\text{WSi}_2$ MATRIX

Fig. 4. K. Sadananda and C.R. Feng

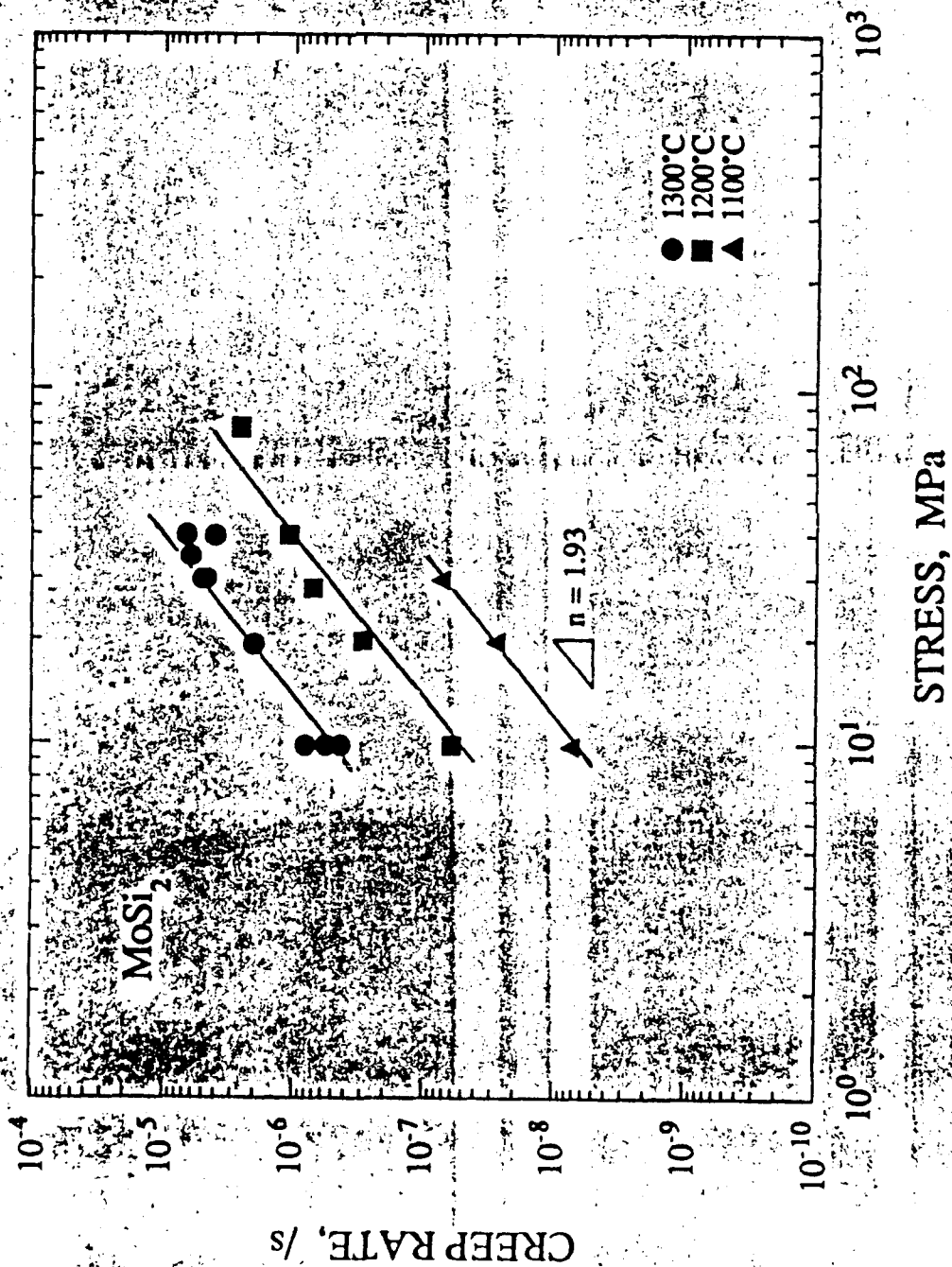


Fig. 5

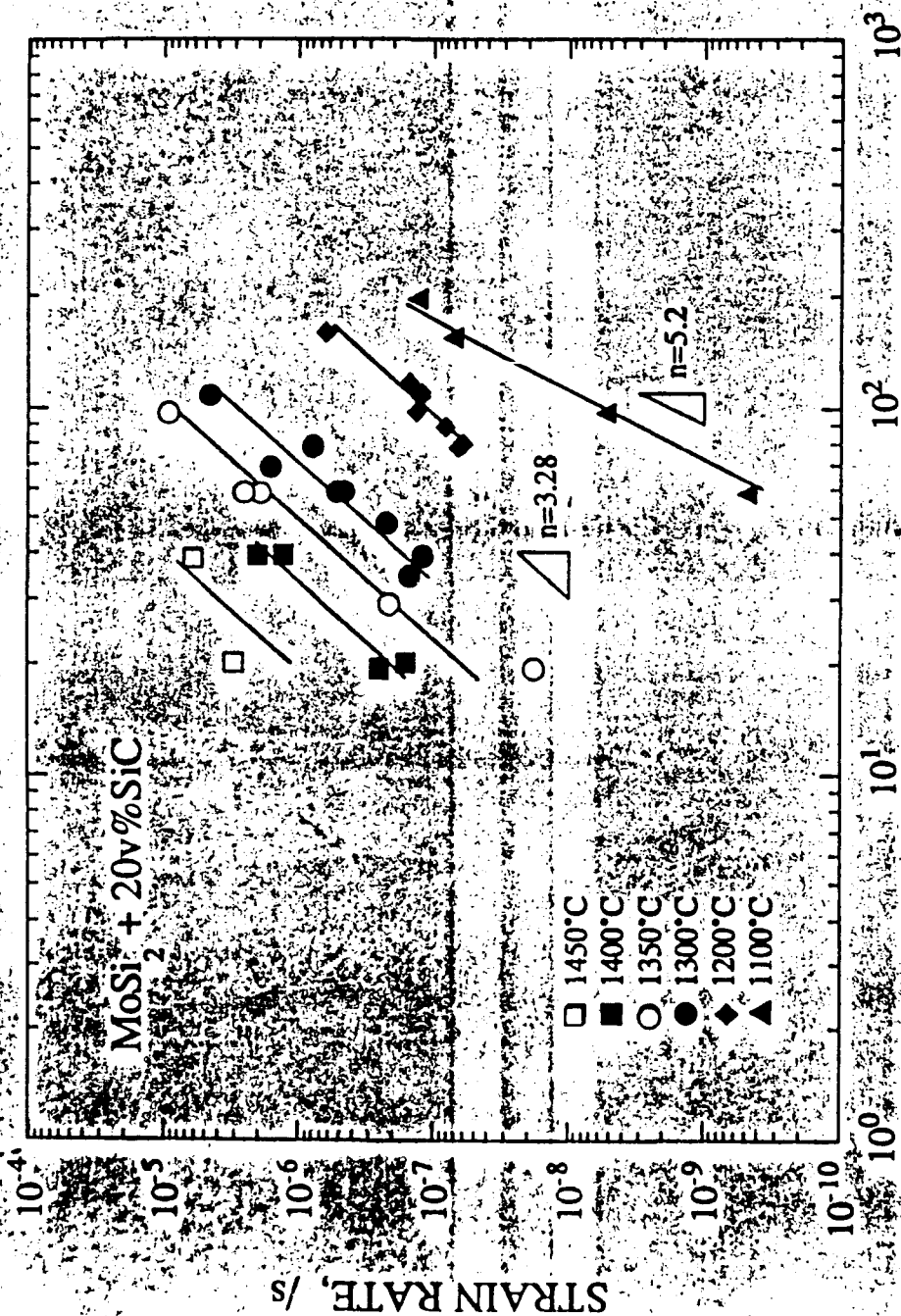
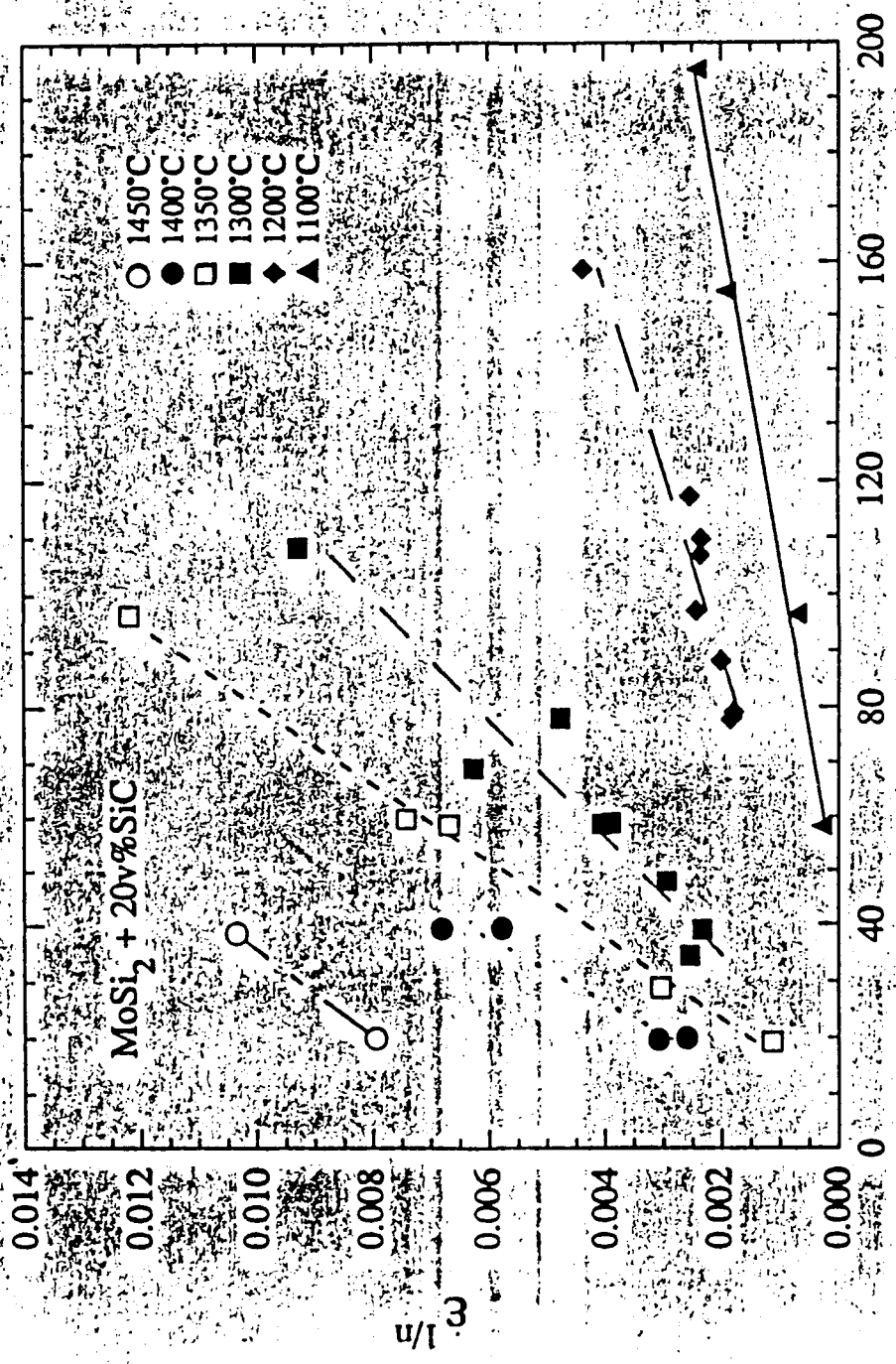
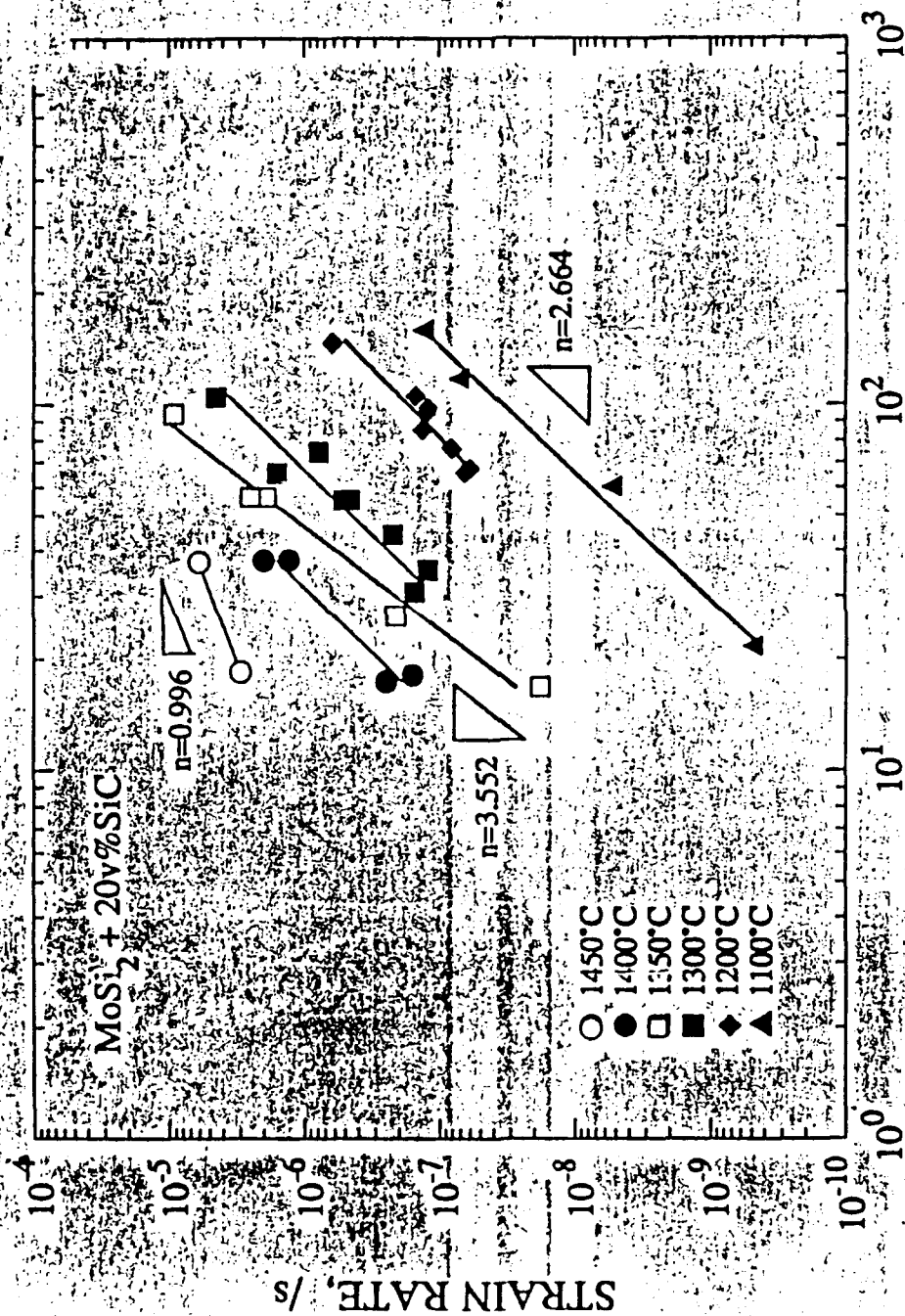


Fig 10

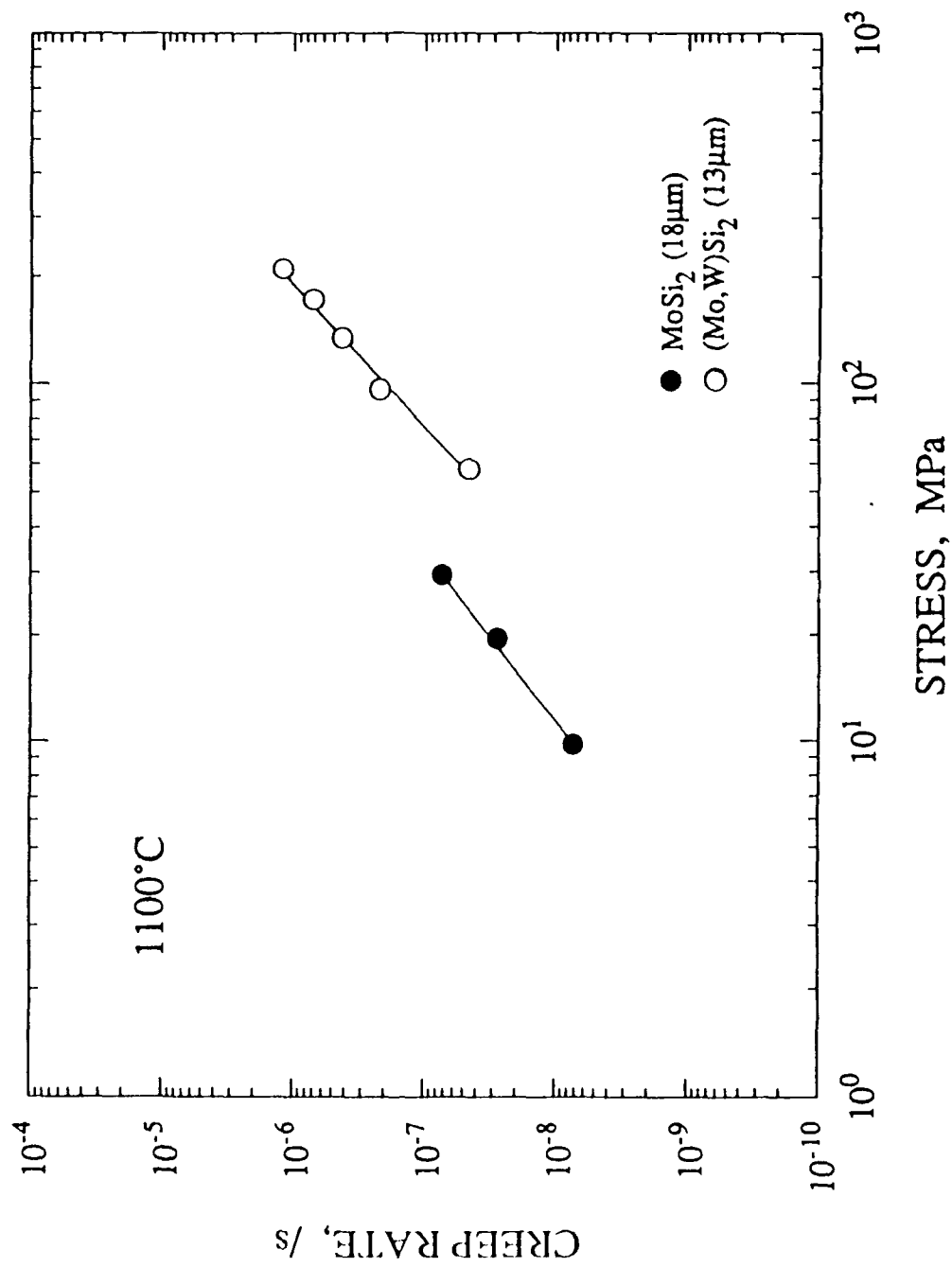


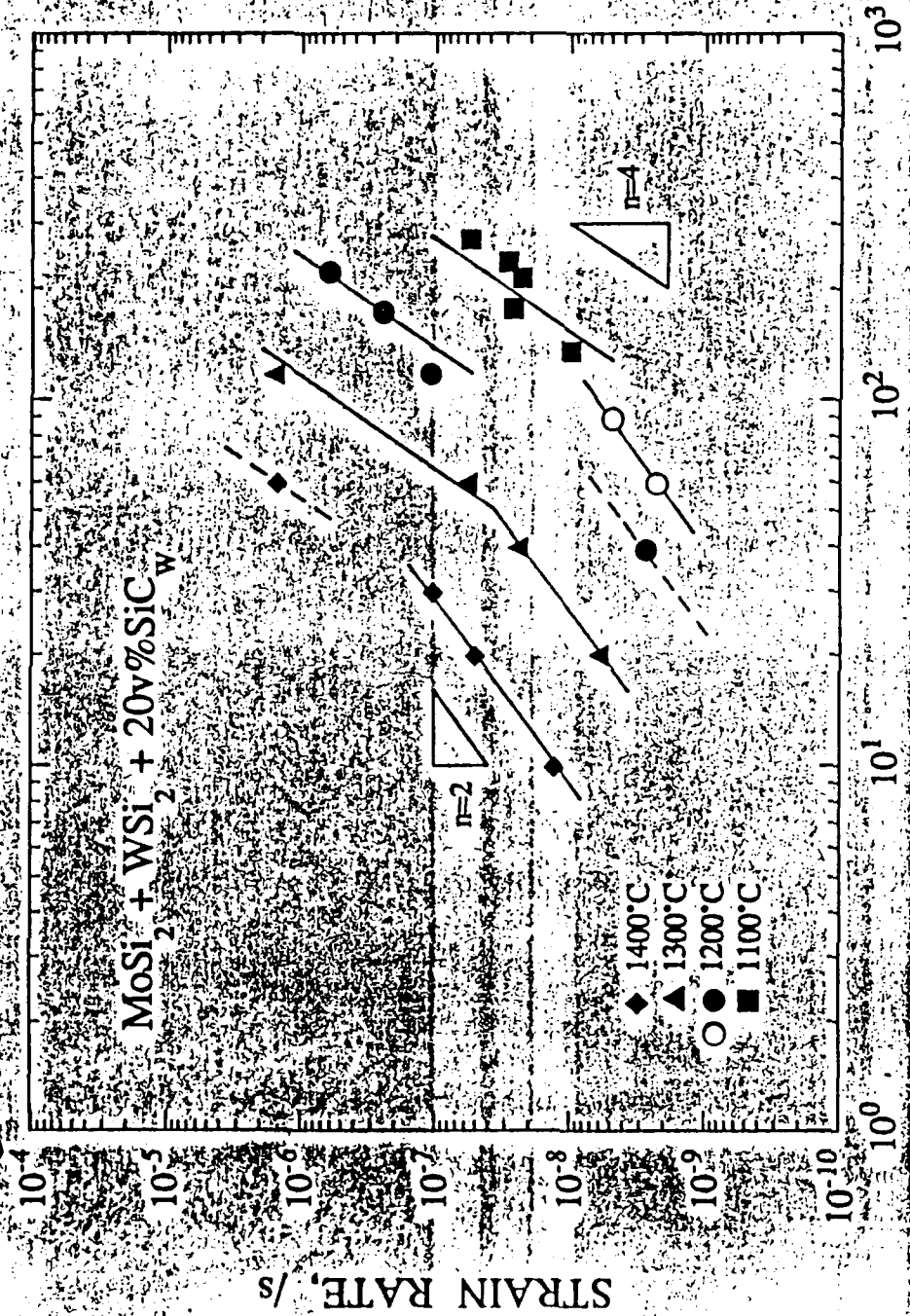
STRESS, MPa

1596-
1556



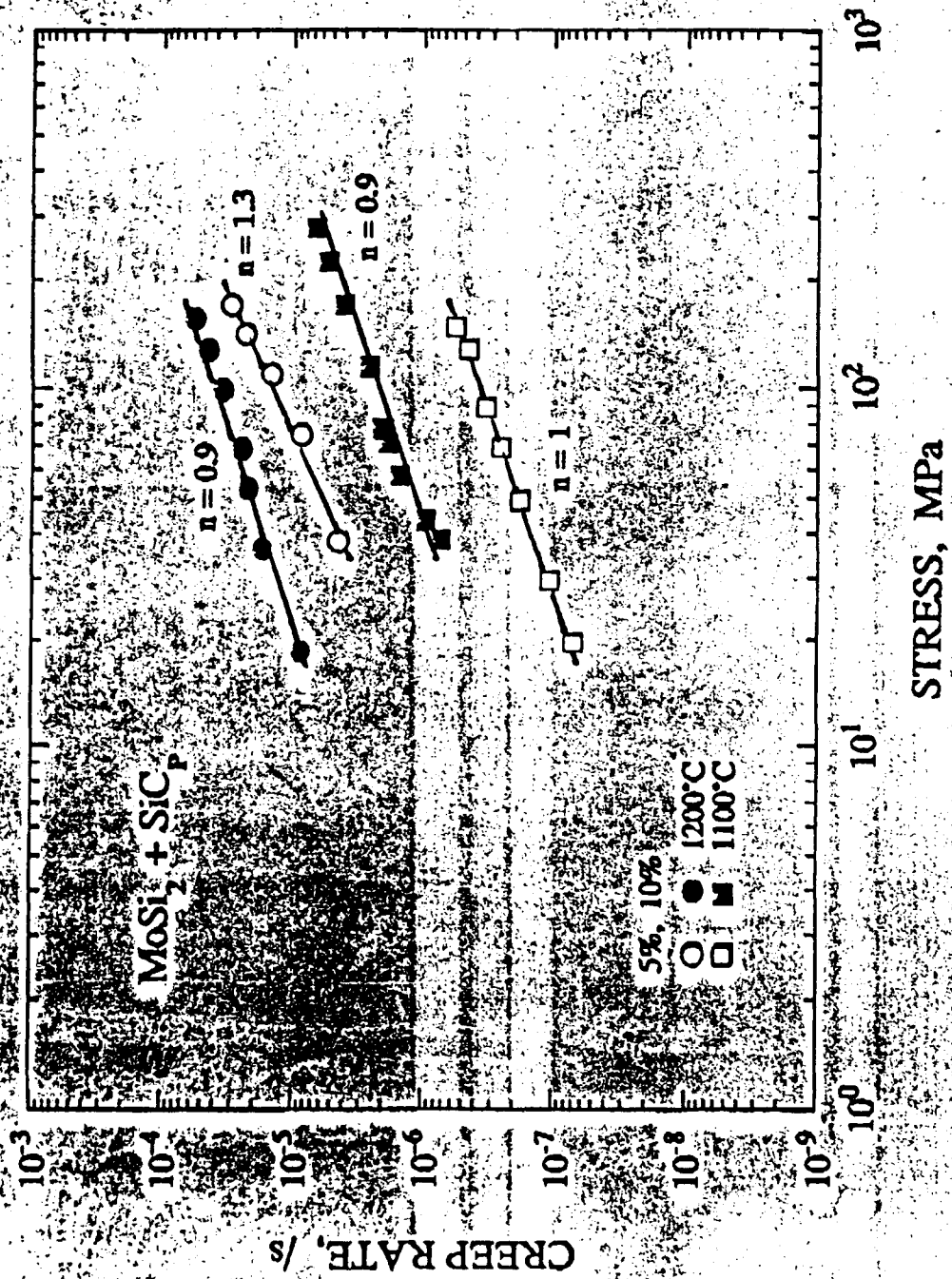
EFFECTIVE STRESS, MPa





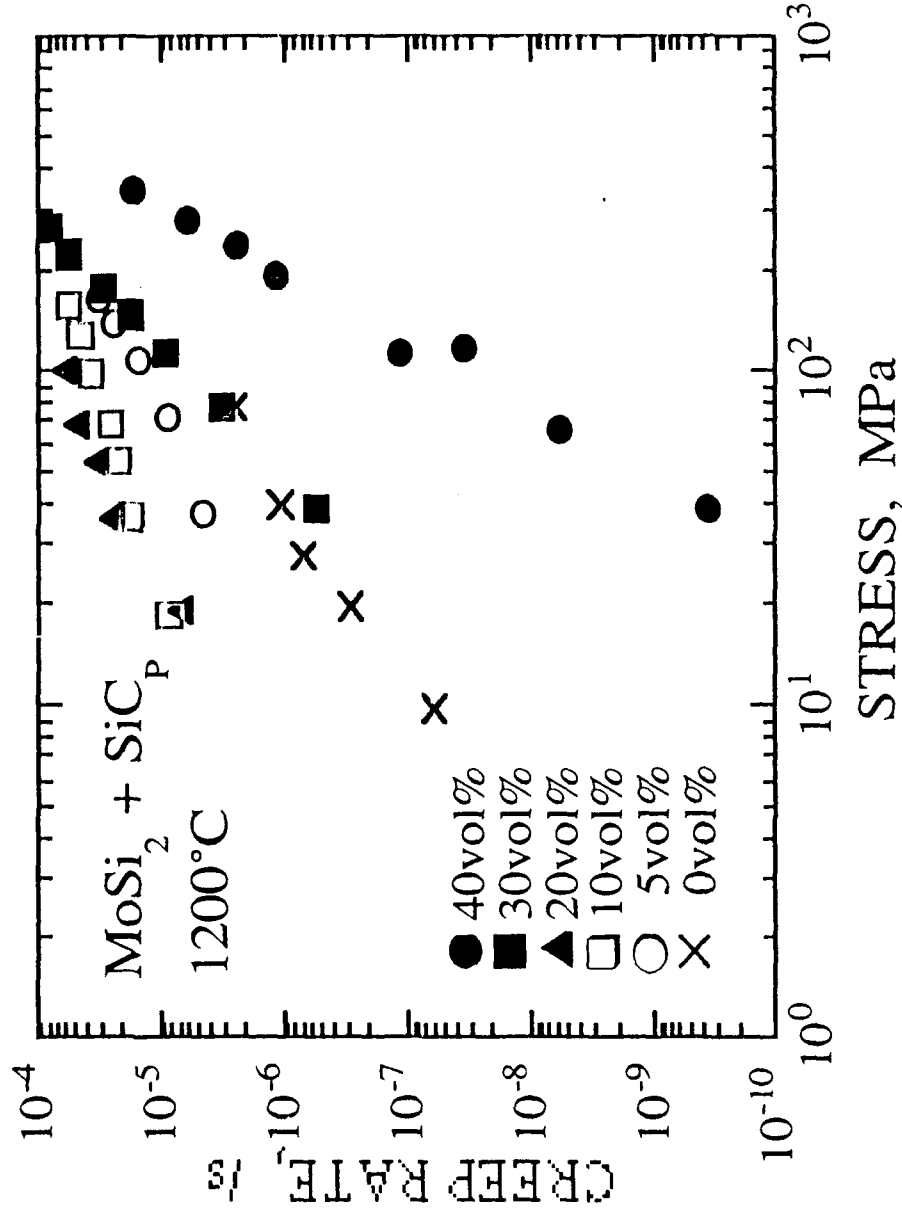
STRESS, MPa

Fig. 5/ K. Sadananda and C.R. Feng



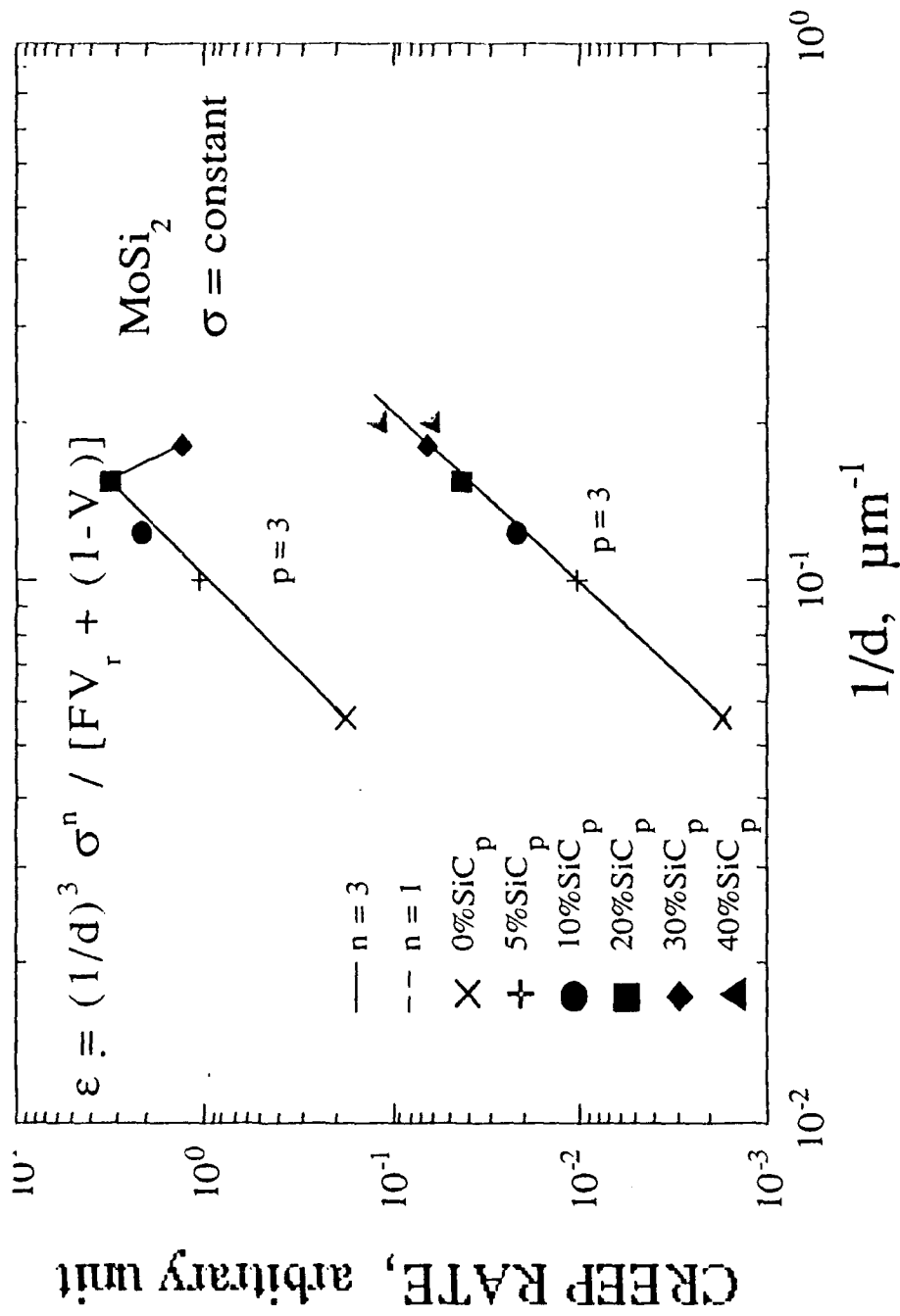
MOLYDISILICIDE WITH SIC PARTICULATES

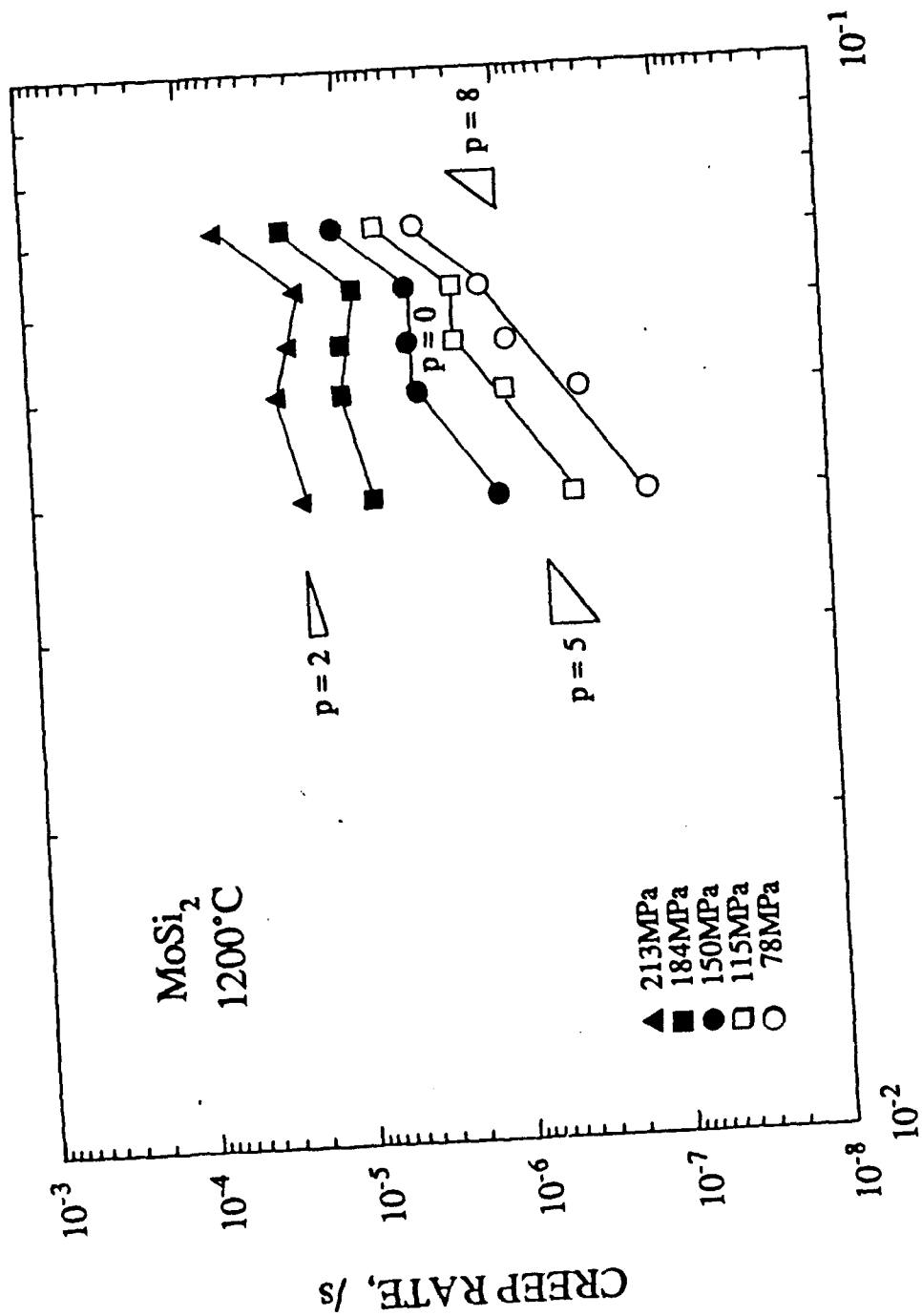
INCREASE AND THEN DECREASE IN CREEP RATES
WITH INCREASE IN VOLUME FRACTION OF SIC



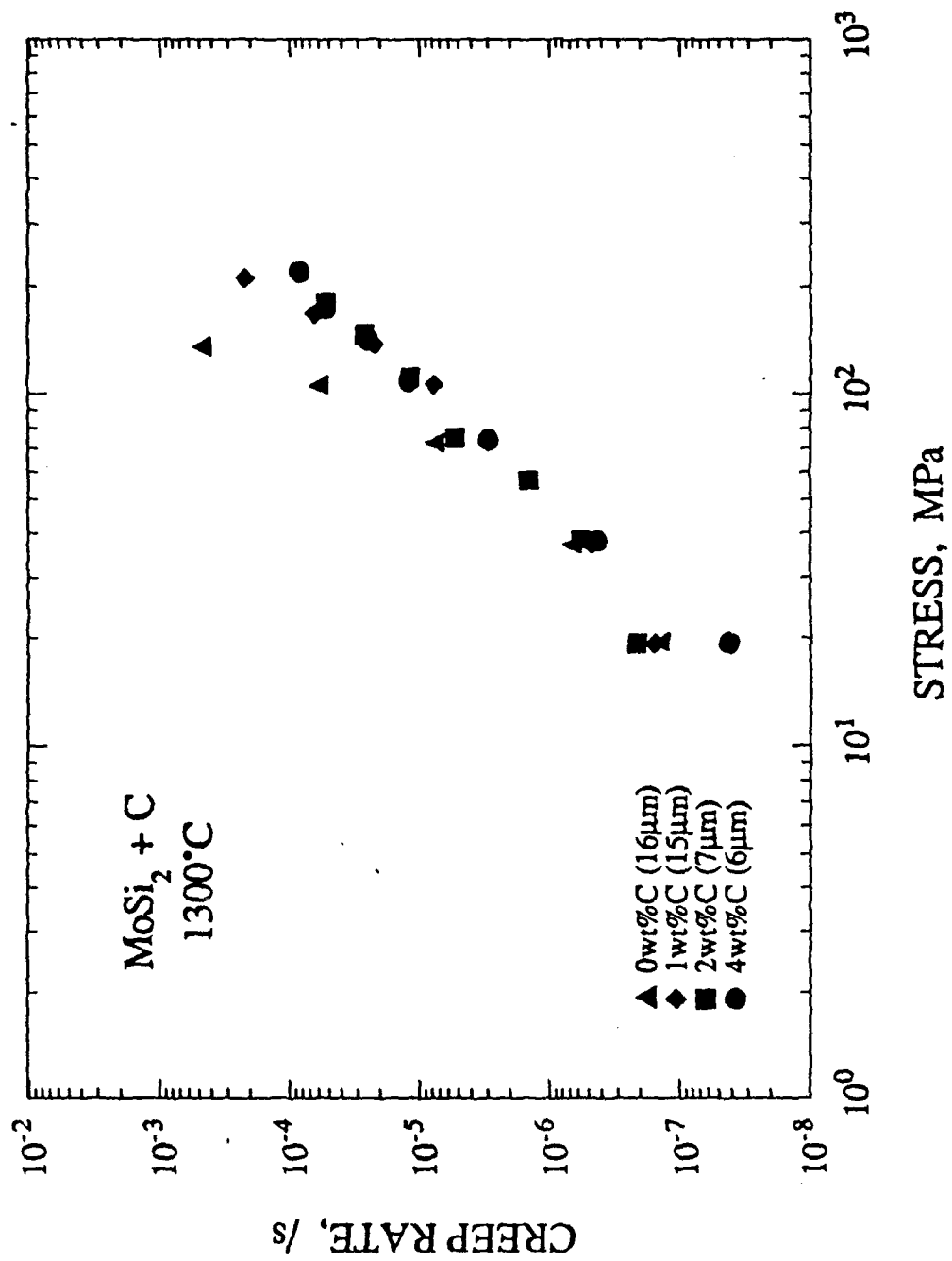
COMBINED EFFECT OF GRAIN SIZE AND VOLUME FRACTION

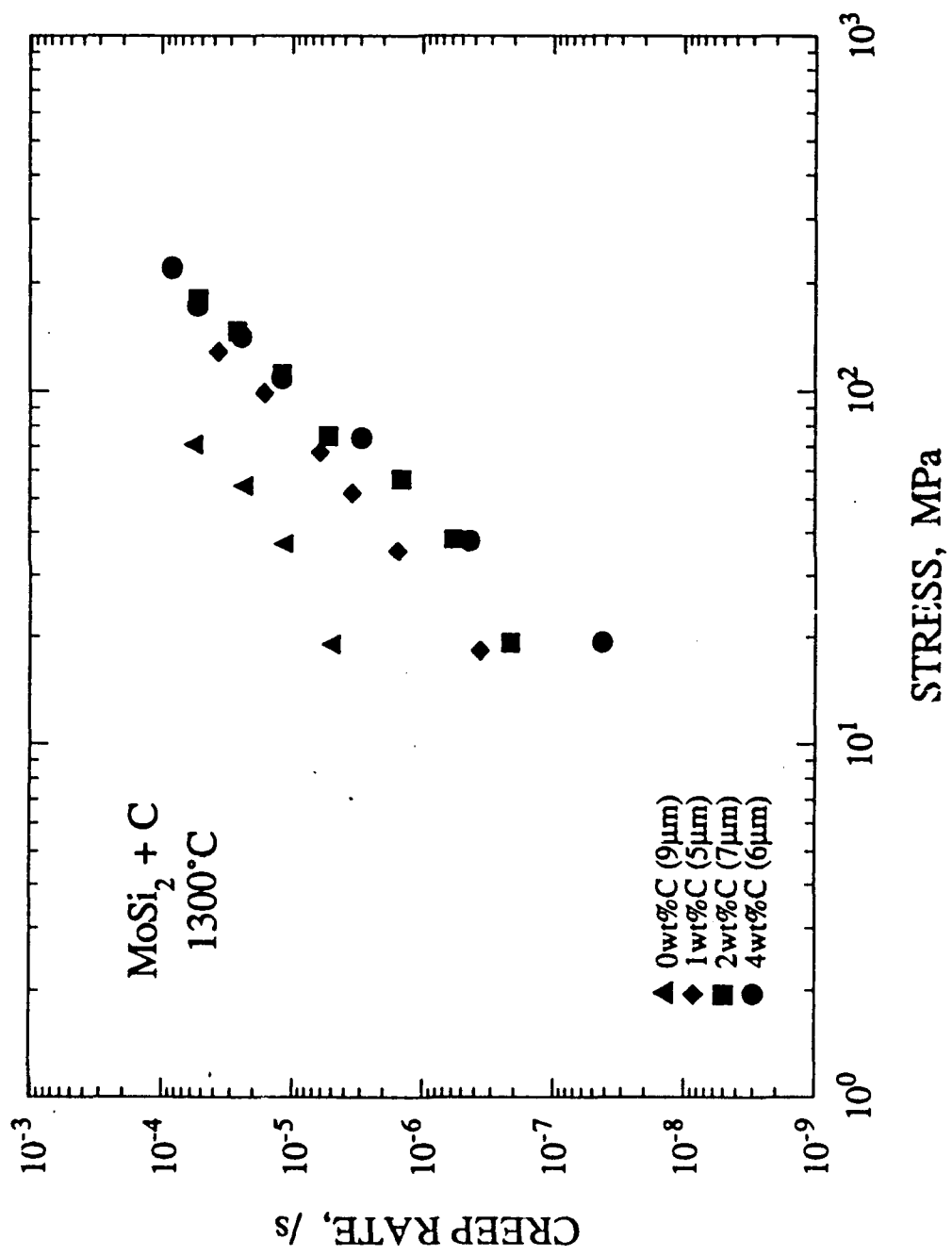
MODIFIED KELLEY & STREET MODEL CONSIDERING GRAIN SIZE EFFECTS - ARISING FROM COBEL CREEP PROCESS

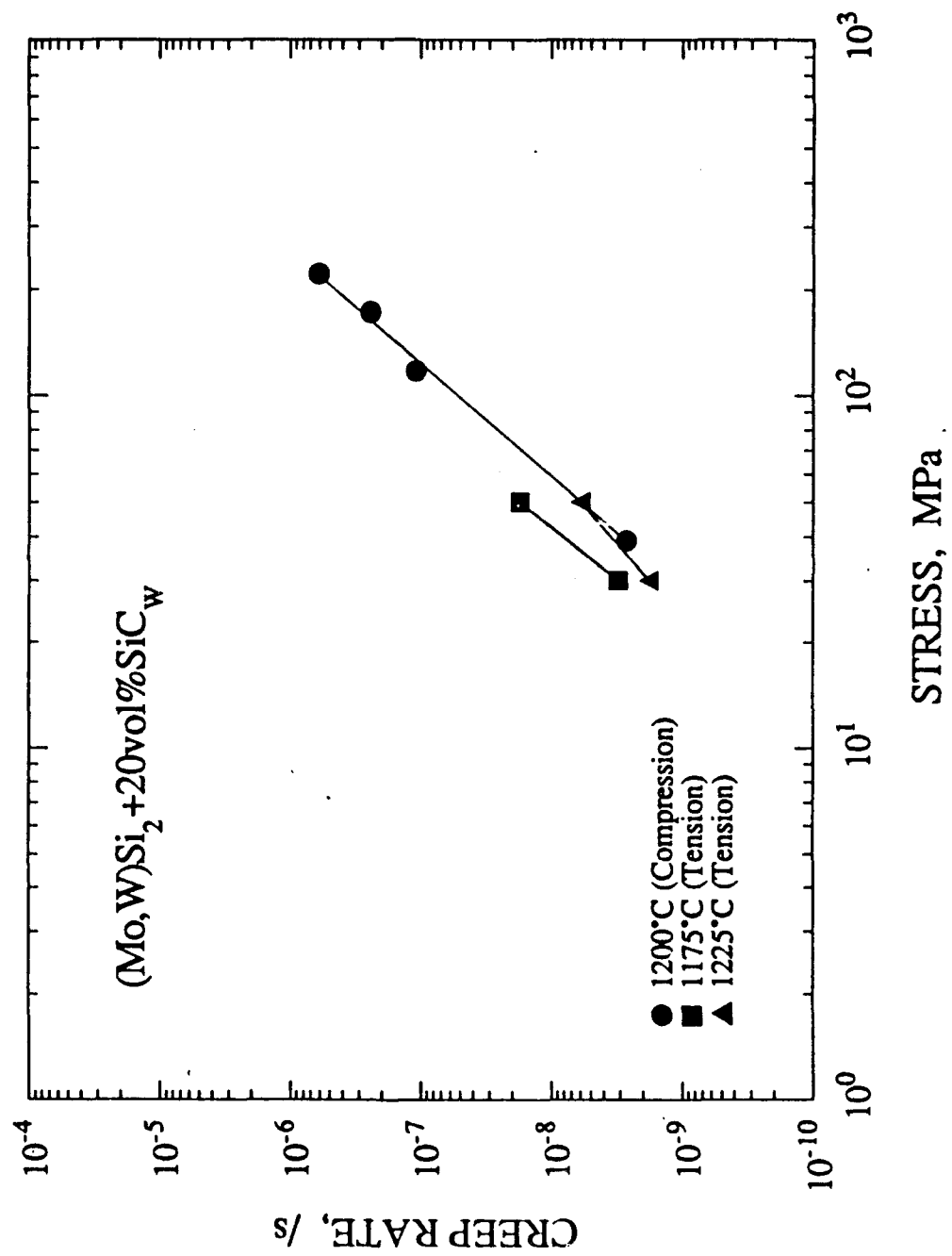


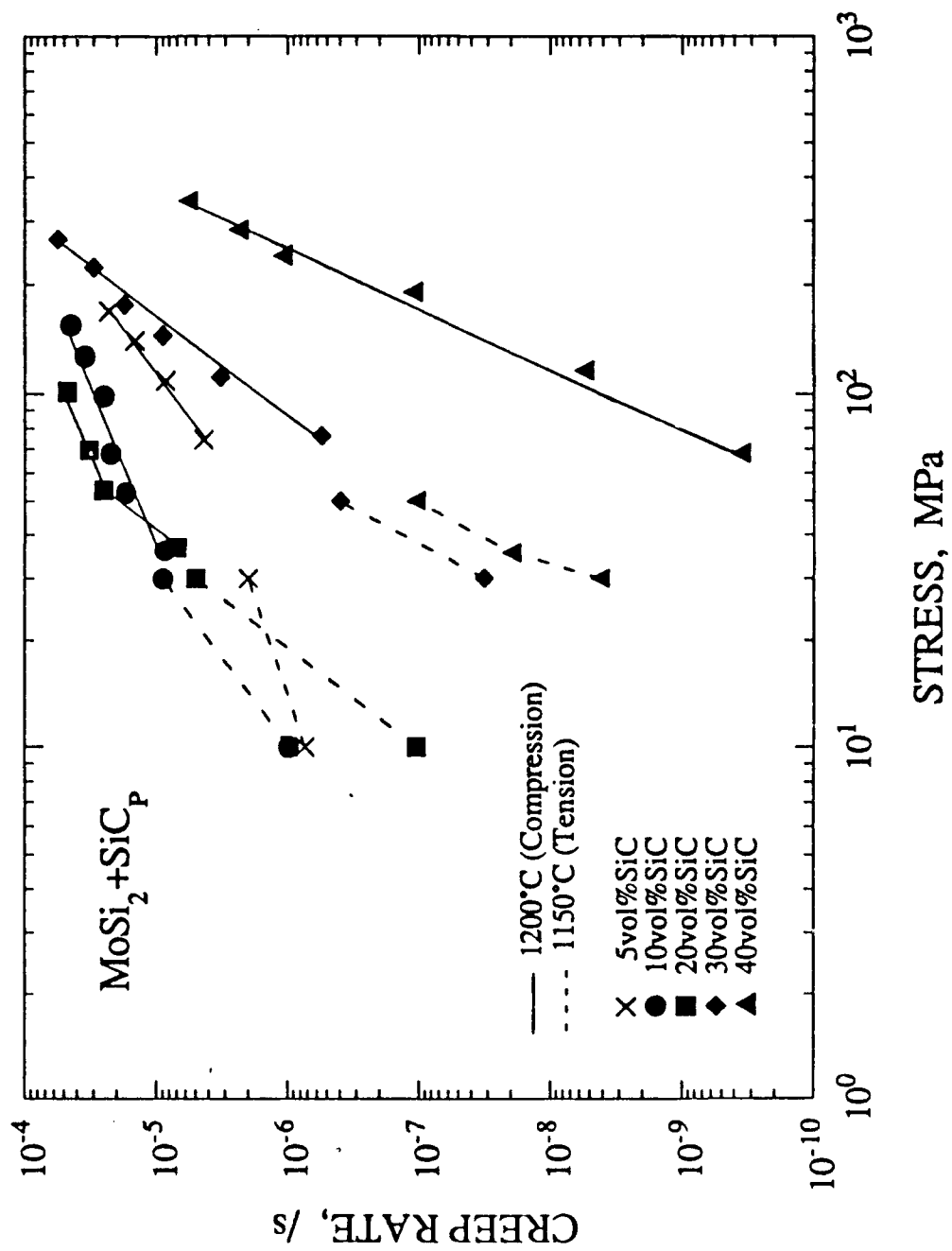


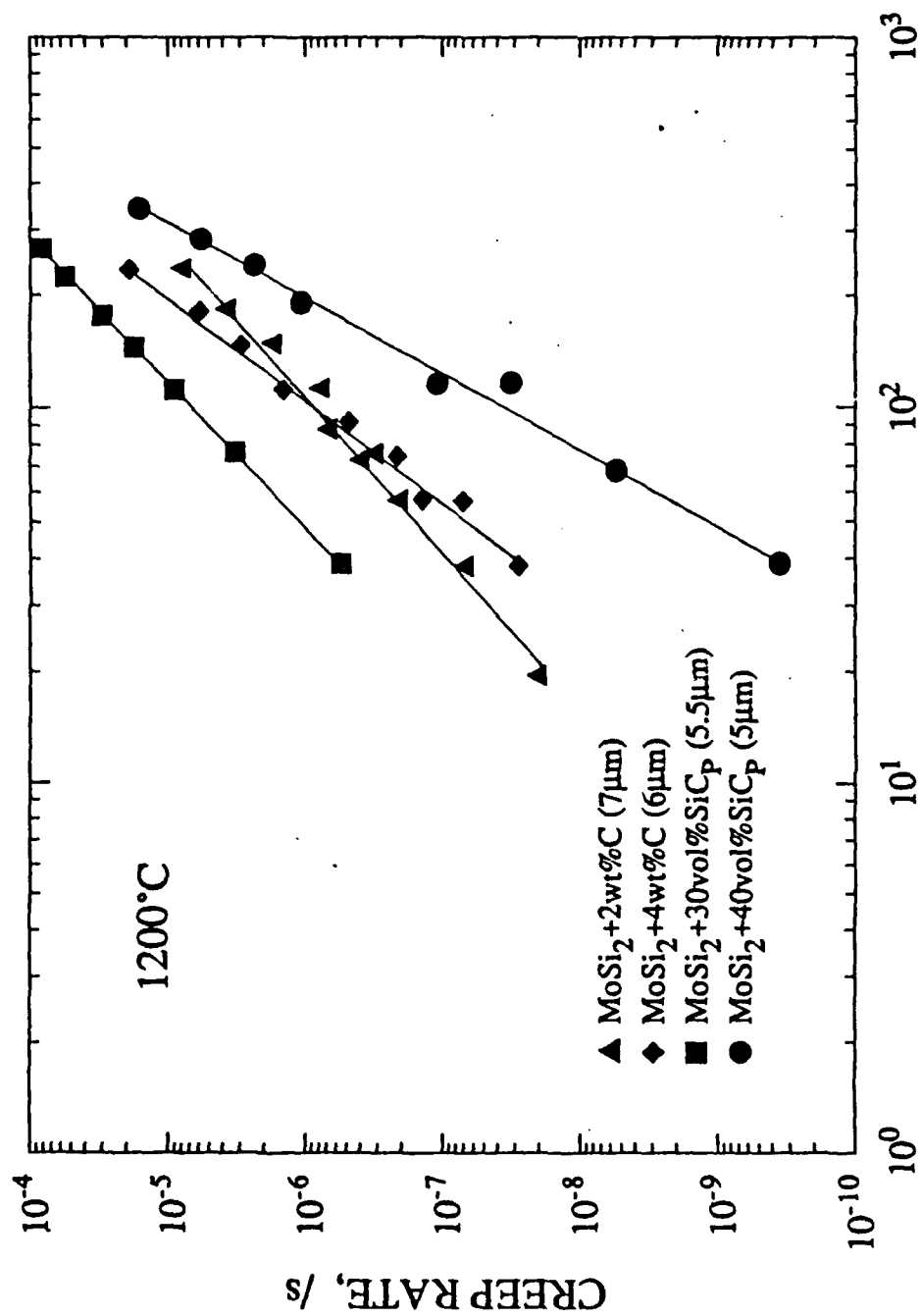
1/d, 1/μm





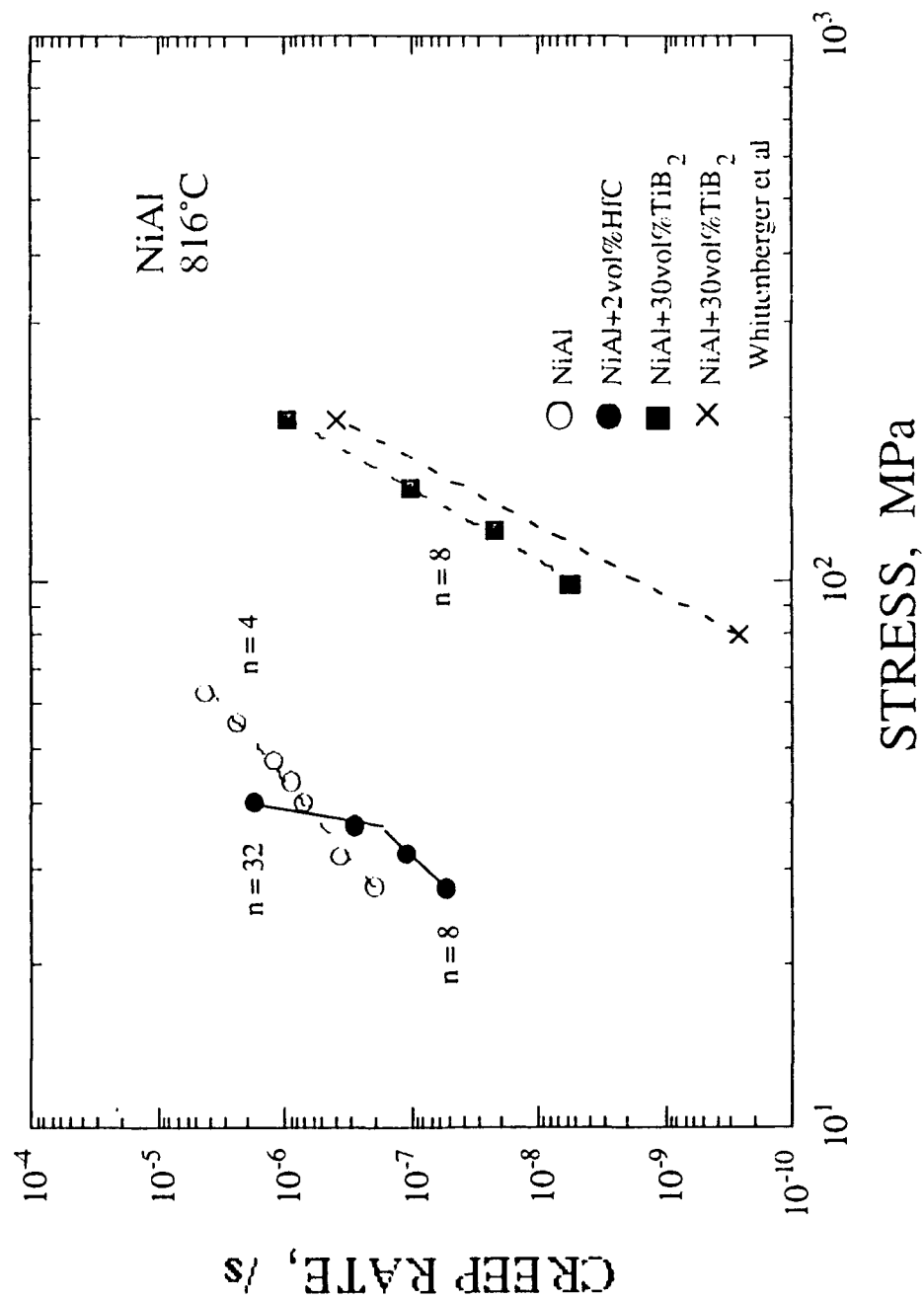






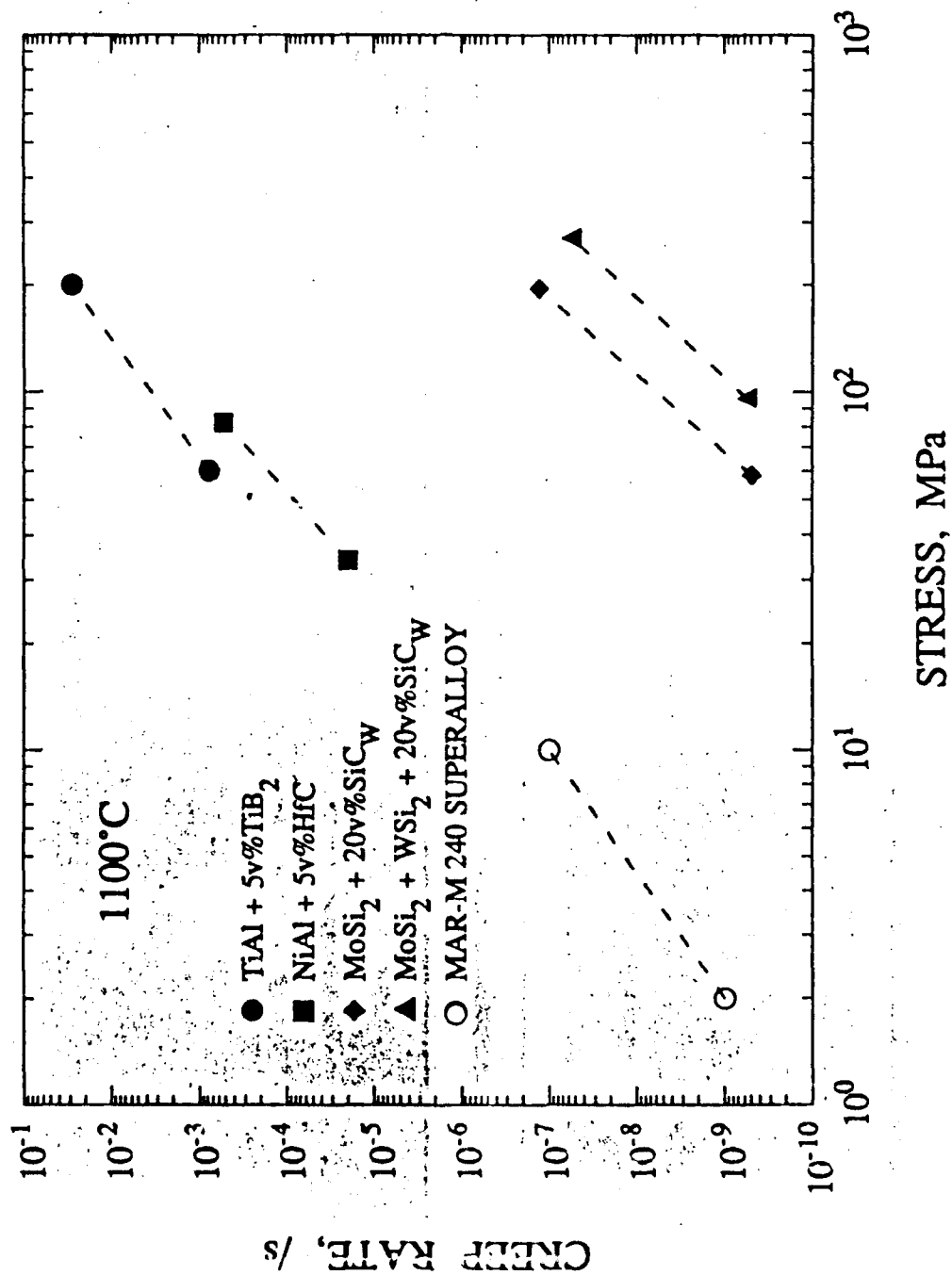
CREEP OF NiAl WITH DISPERSOIDS AND REINFORCEMENTS

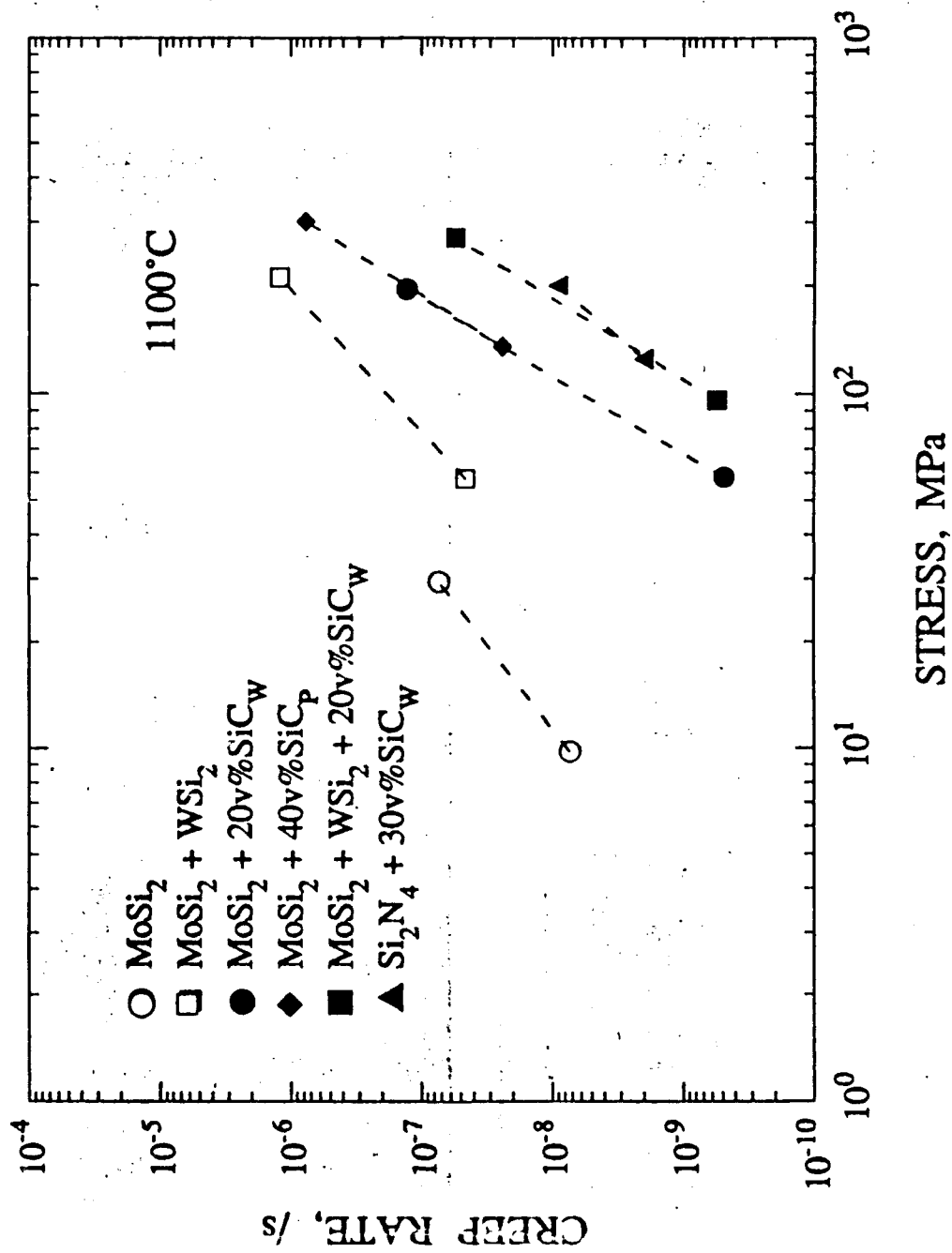
HIGH VOLUME FRACTION OF REINFORCEMENT REQUIRED TO ENHANCE CREEP RESISTANCE





TEM MICROGRAPHS OF $\text{MoSi}_2 + 20\text{vol}\% \text{SiC}$
DEFORMED BY CREEP AT 1200°C AND AT 11.5ksi





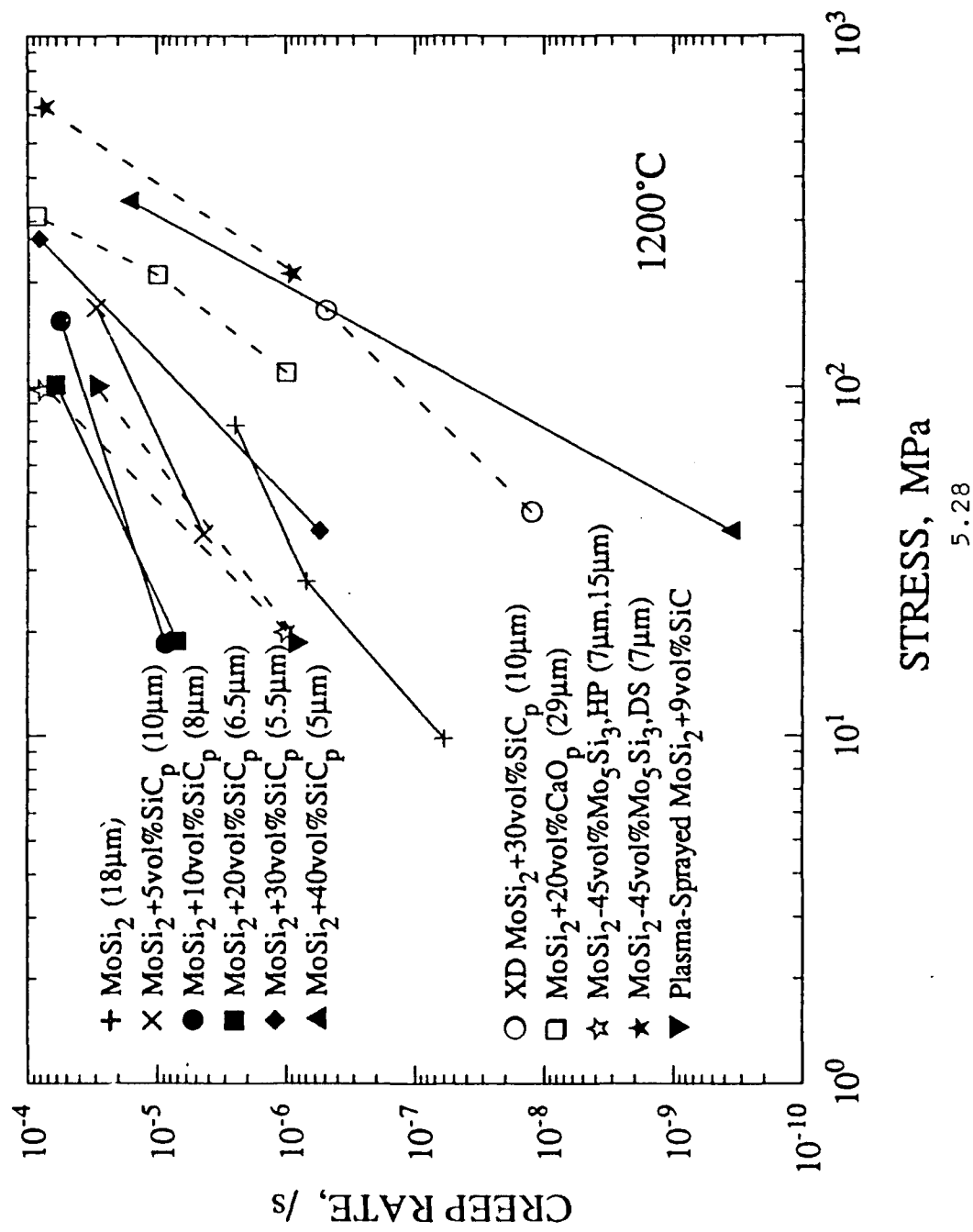


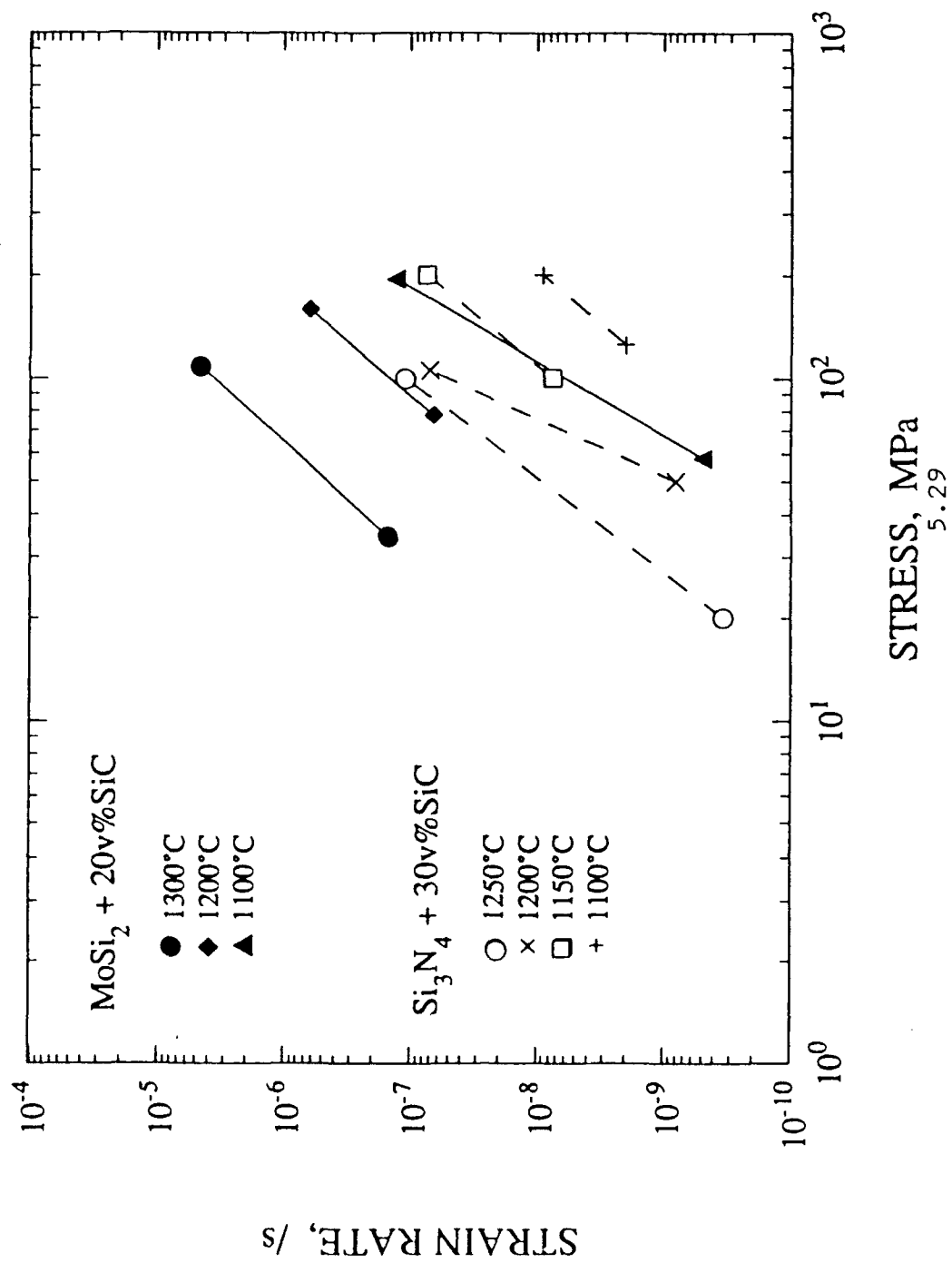
TEM MICROGRAPH OF MoSi_2
DEFORMED BY CREEP AT 1200°C AND AT 11.5ksi



MoSi₂ + 20vol% SiC

TEM MICROGRAPHS OF MoSi₂ + 20vol% SiC
(undeformed)





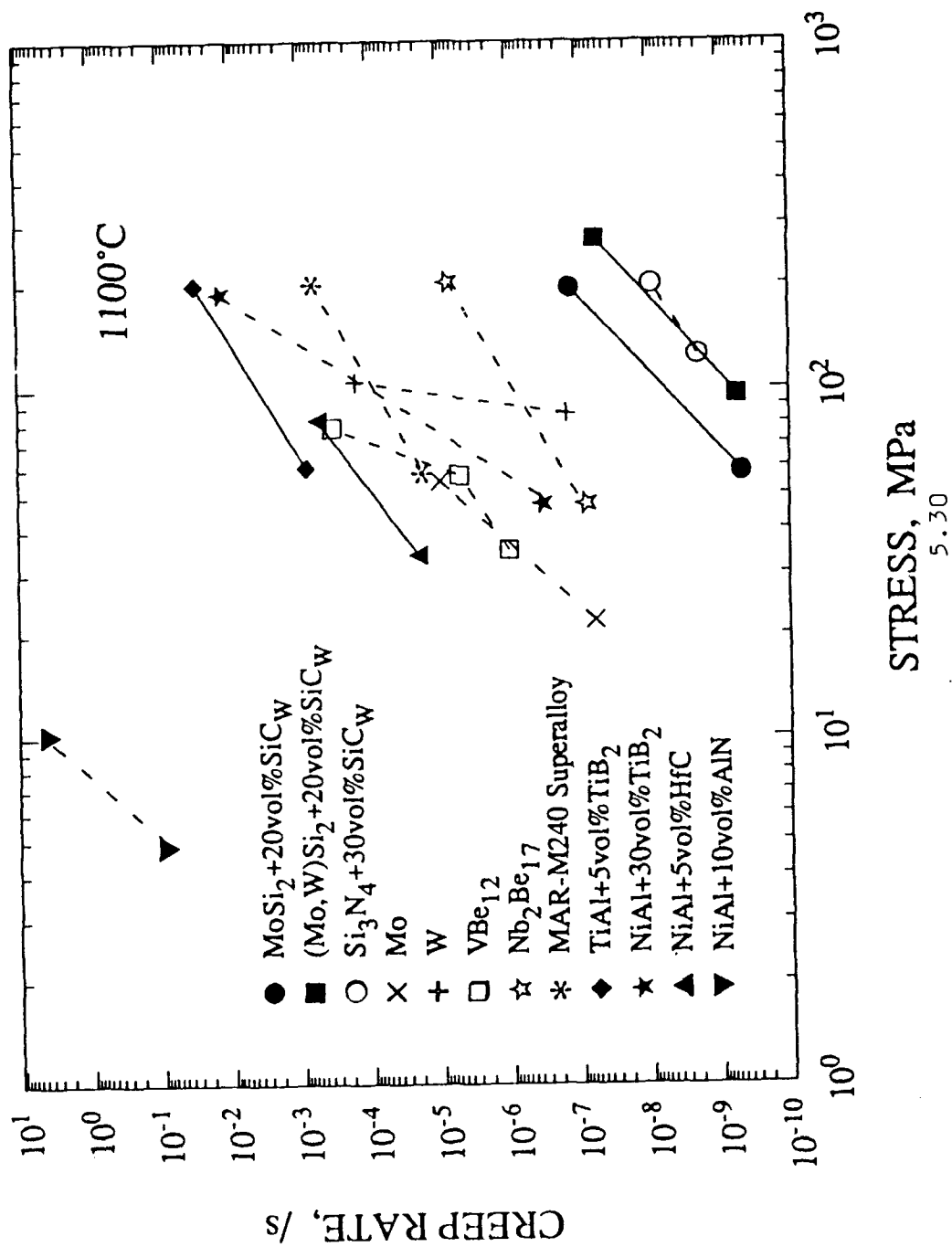
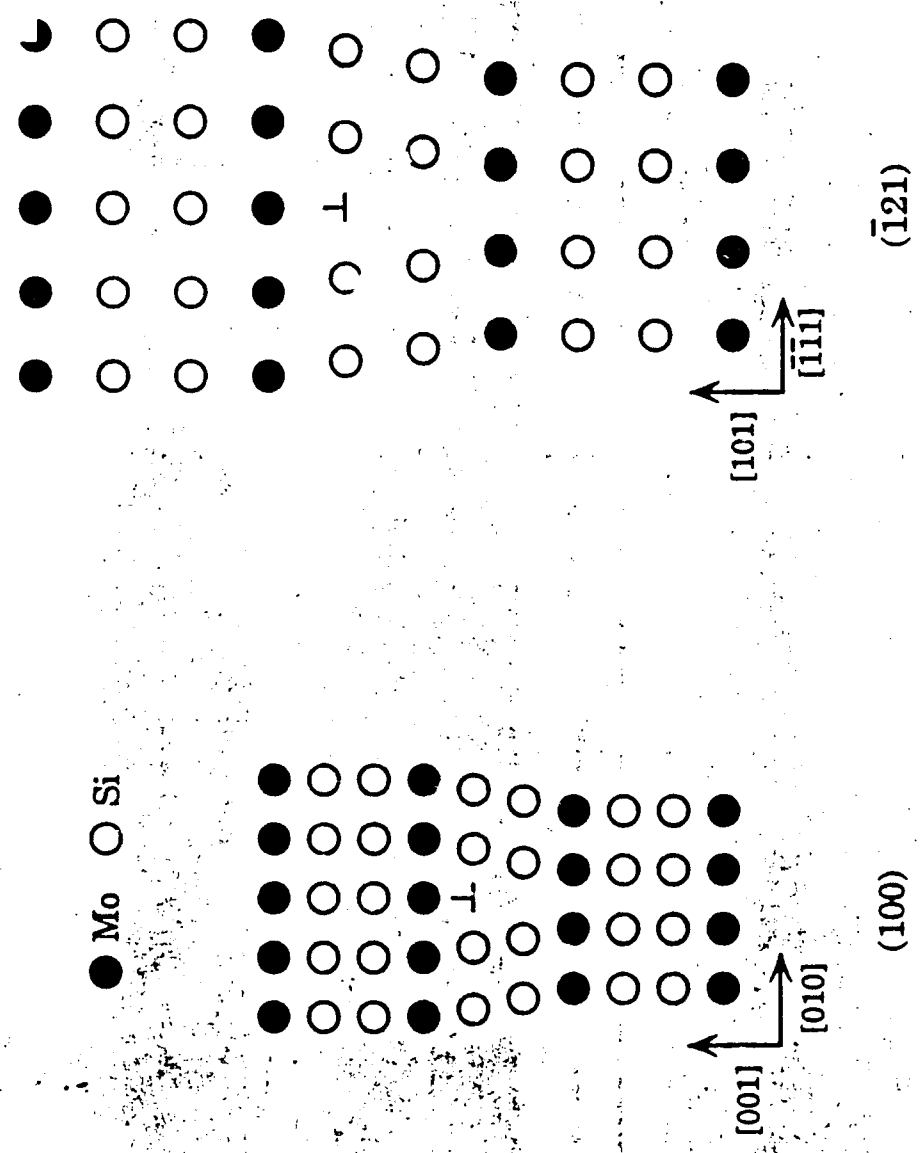


Fig 21



SUMMARY AND CONCLUSIONS

CREEP DEFORMATION BEHAVIOR OF ALUMINIDES AND SILICIDES AND THEIR COMPOSITES.

SIGNIFICANT IMPROVEMENT IN CREEP RESISTANCE BY REINFORCEMENT.

IN ALL CASES THE REINFORCEMENTS DEFORMS MOSTLY ELASTICALLY AT THE TEMPERATURES AND STRESSES INVESTIGATED.

ROLE OF BACK STRESSES OR INTERNAL STRESSES IN THESE MATERIALS ARE INSIGNIFICANT.

RATE CONTROLLING PROCESSES ARE PREDOMINANTLY CLIMB RELATED.

MOLYDISILICIDES ARE FAR SUPERIOR TO ALUMINIDES AND SUPERALLOYS IN TERMS OF CREEP RESISTANCE AT $T > 1000^{\circ}\text{C}$.

CONCLUSIONS

- * Creep resistance of molybdisilicides for superior to superalloys and intermetallic composites
- * Grain size effects are very significant even in power-law creep regime
- * Creep strengths of MoSi_2 Composites comparable to ceramic-ceramic systems
- * Efforts should now be concentrated in enhancing low temperature toughness

6. Ordered Ground State Structures in HCP Alloys

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and

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ORDERED GROUND STATE STRUCTURES IN HCP ALLOYS

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Institute of Technology
Banaras Hindu University
VARANASI-221005, India

THERMODYNAMIC STABILITY

**ORDERED
GROUND
STATE
STRUCTURES**

**ORDERING
FROM
ENTROPY
CONSIDERATIONS**

GROUND STATE STRUCTURES

CONFIGURATION ENERGY

$$E = \sum_j (1/2) q_j W_j$$

q_j : number of j th neighbour A-B bonds

$$W_j : 2V_{AB}^j - V_{AA}^j - V_{BB}^j = \text{Interchange energy}$$

For third neighbour interaction

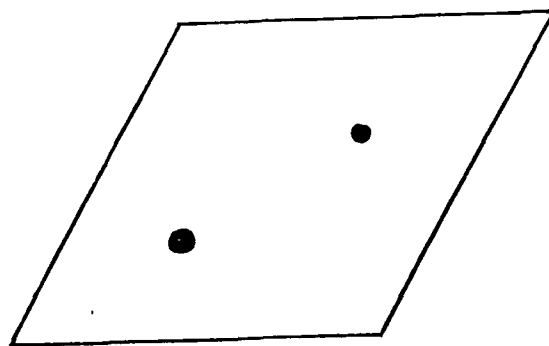
$$E = (1/2) (q_1 W_1 + q_2 W_2 + q_3 W_3)$$

$$E/W = (1/2) (q_1 + q_2 v_1 + q_3 v_2)$$

$$\text{where : } v_1 = W_2/W_1 \quad \text{and } v_2 = W_3/W_1$$

- DETAILS OF HCP STRUCTURE

- SPACE GROUP $P6_3/mmc$



- ATOMIC POSITIONS

2C $\bar{6}m2$ $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$; $\frac{2}{3}, \frac{1}{3}, \frac{3}{4}$

- CO-ORDINATION NUMBER 6 : 6 : 6

- IDEAL AND NON-IDEAL AXIAL RATIO

GENERAL ASSUMPTIONS:

- BINARY ALLOY

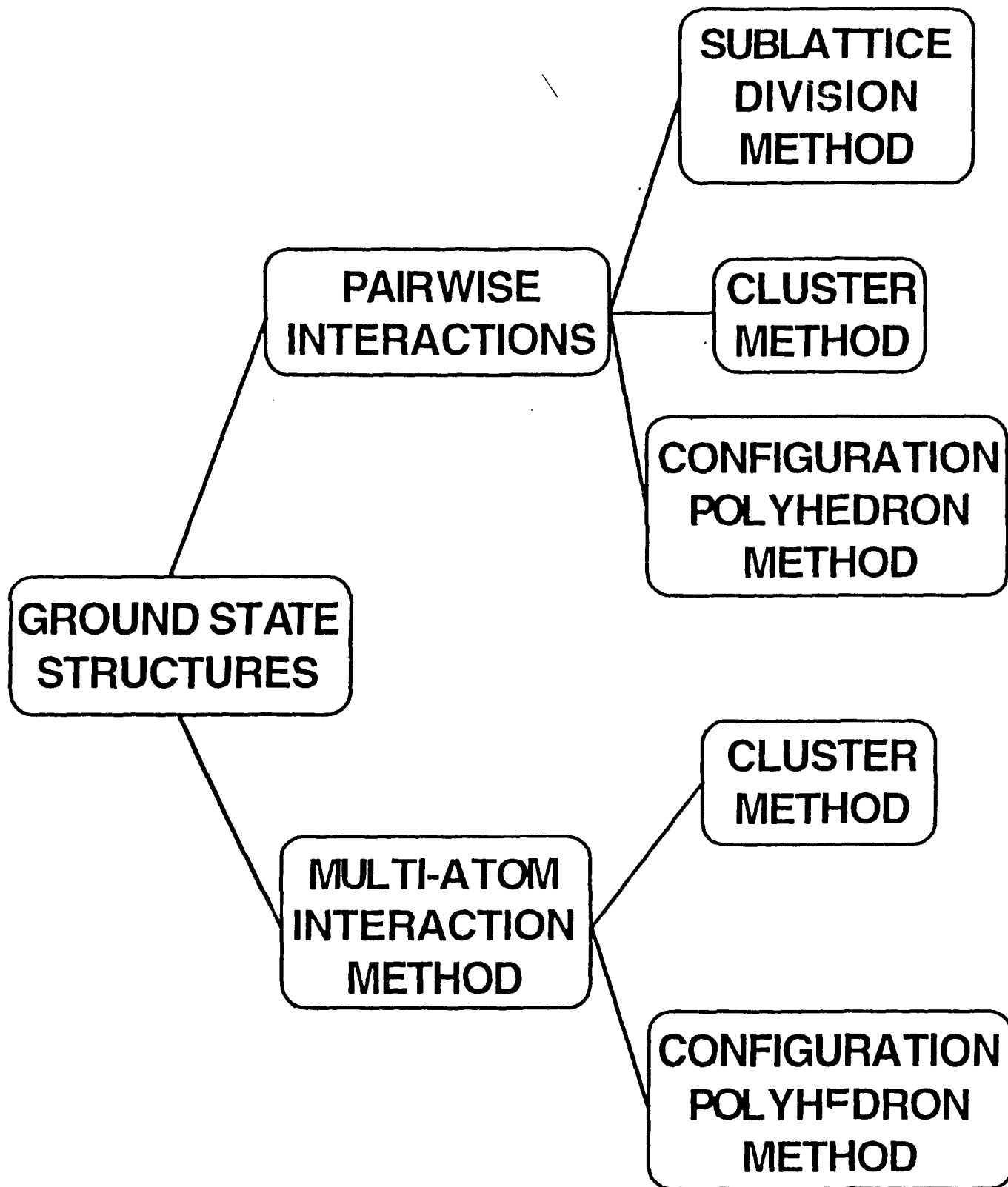
- NON-IDEAL AXIAL RATIO

PAIRWISE INTERACTIONS UPTO THIRD NEIGHBOUR

- ENERGY IS FUNCTION OF PAIRWISE INTERACTIONS ONLY

VIBRATIONAL AND SIZE EFFECTS ARE IGNORED

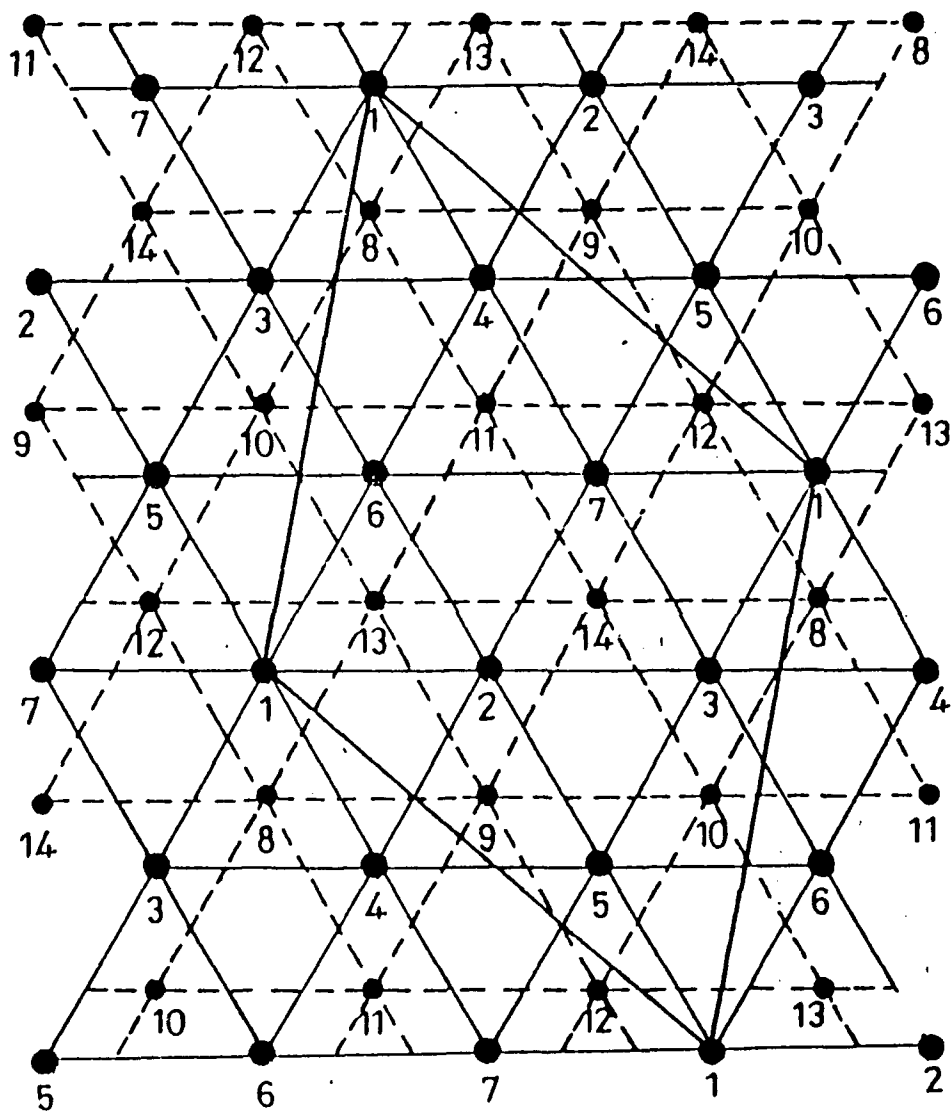
- VACANT SITES ARE NOT ALLOWED

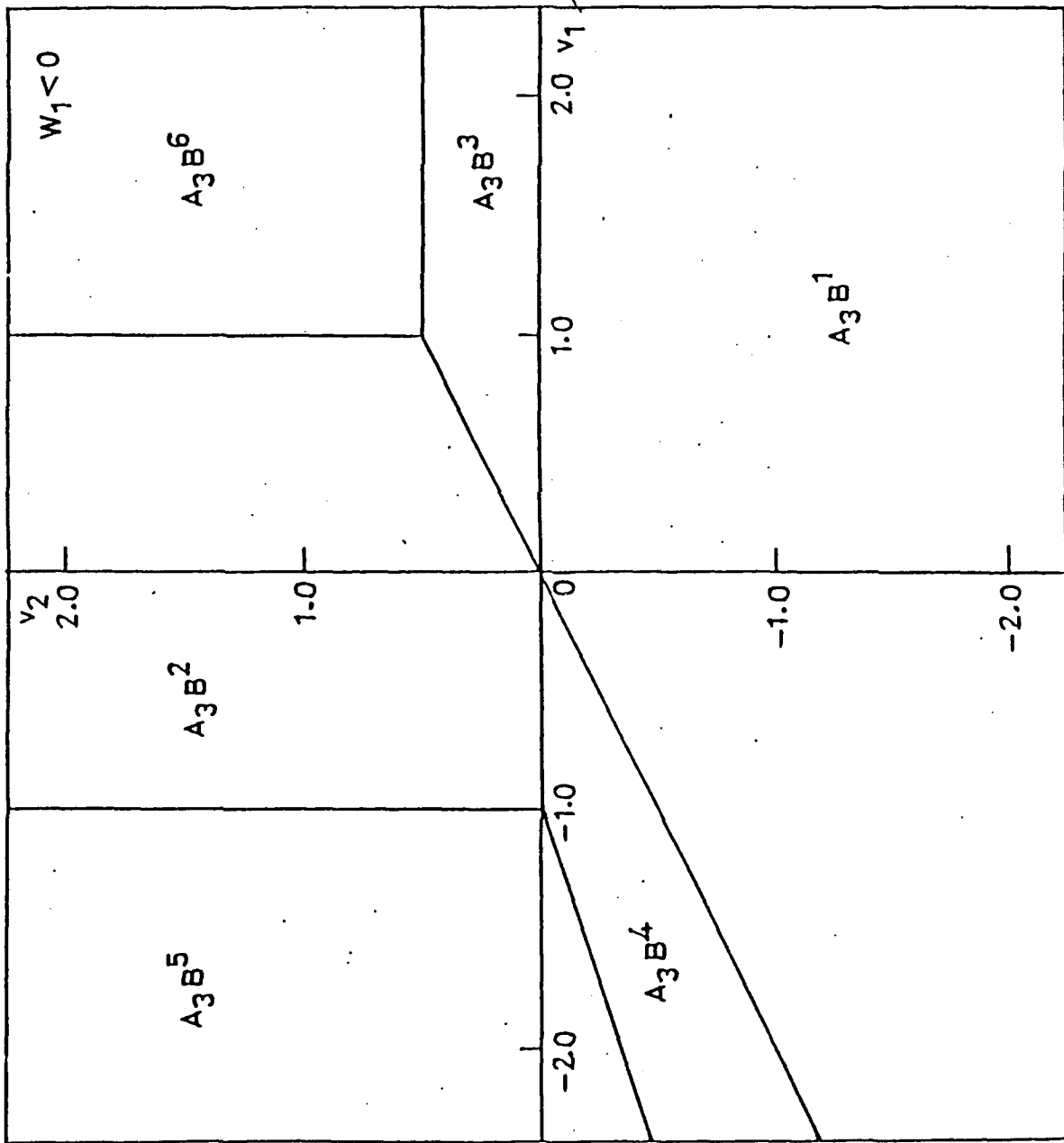


CLASSIFICATION OF DISTINCT LAYER

(7 SUBLATTICES/LAYER

LAYER DESIGNATION	SITES OCCUPIED BY B ATOMS	FRACTION OF B ATOMS IN LAYER
L1	—	0
L2	1	$1/7$
L3	1, 2	$2/7$
L4	1, 2, 3	$3/7$
L5	1, 2, 4	$3/7$
L6	4, 5, 6, 7	$4/7$
L7	3, 5, 6, 7	$4/7$
L8	3, 4, 5, 6, 7	$5/7$
L9	2, 3, 4, 5, 6, 7	$6/7$
L10	1, 2, 3, 4, 5, 6, 7	1

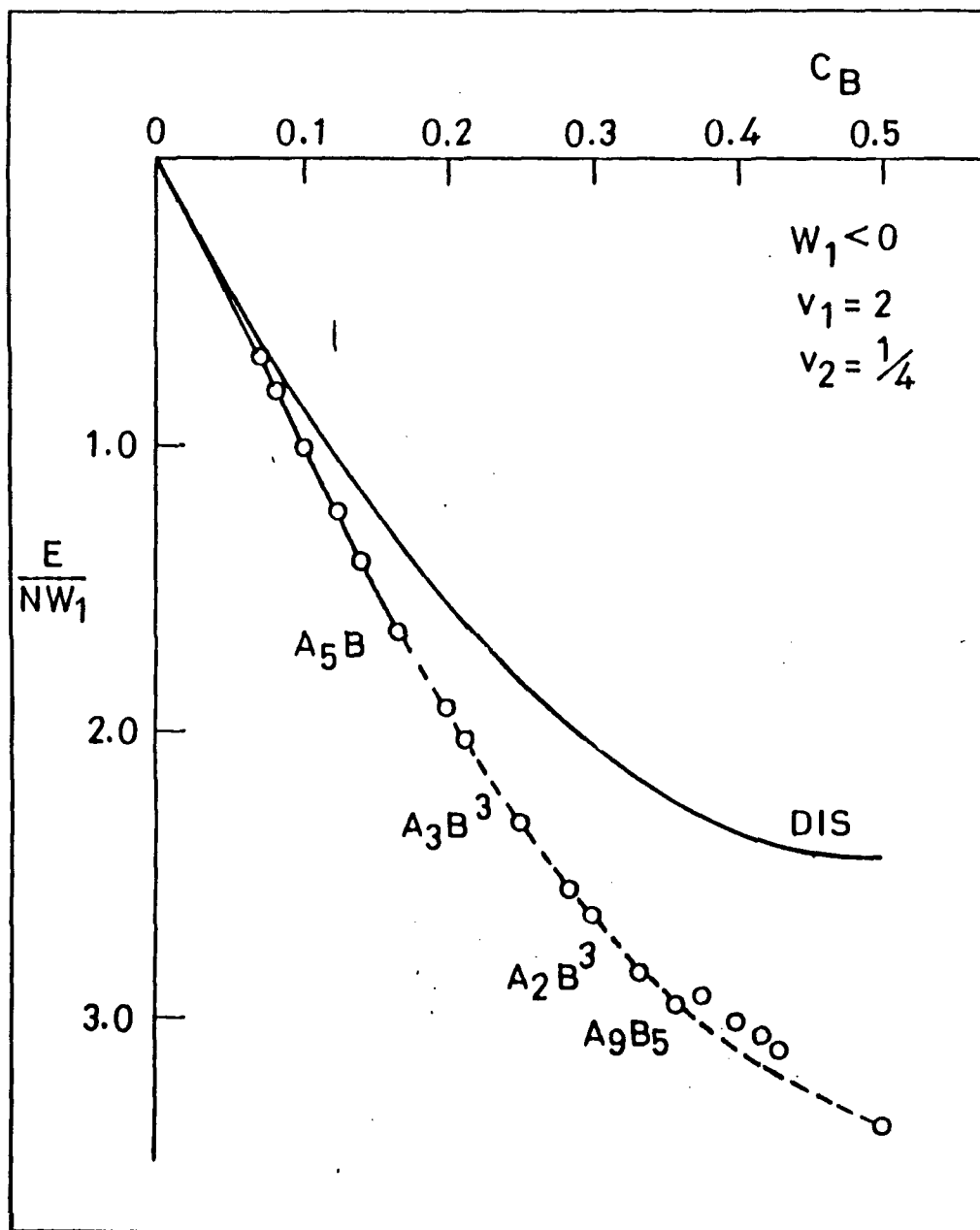


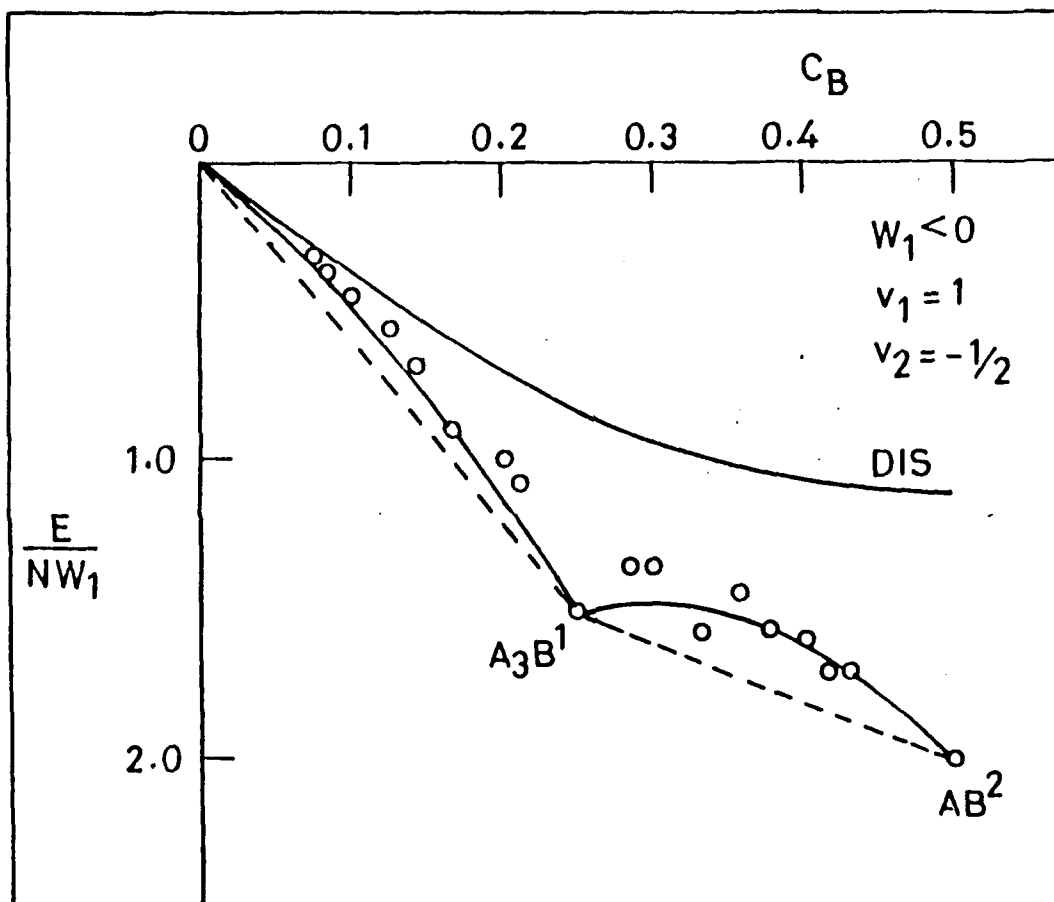


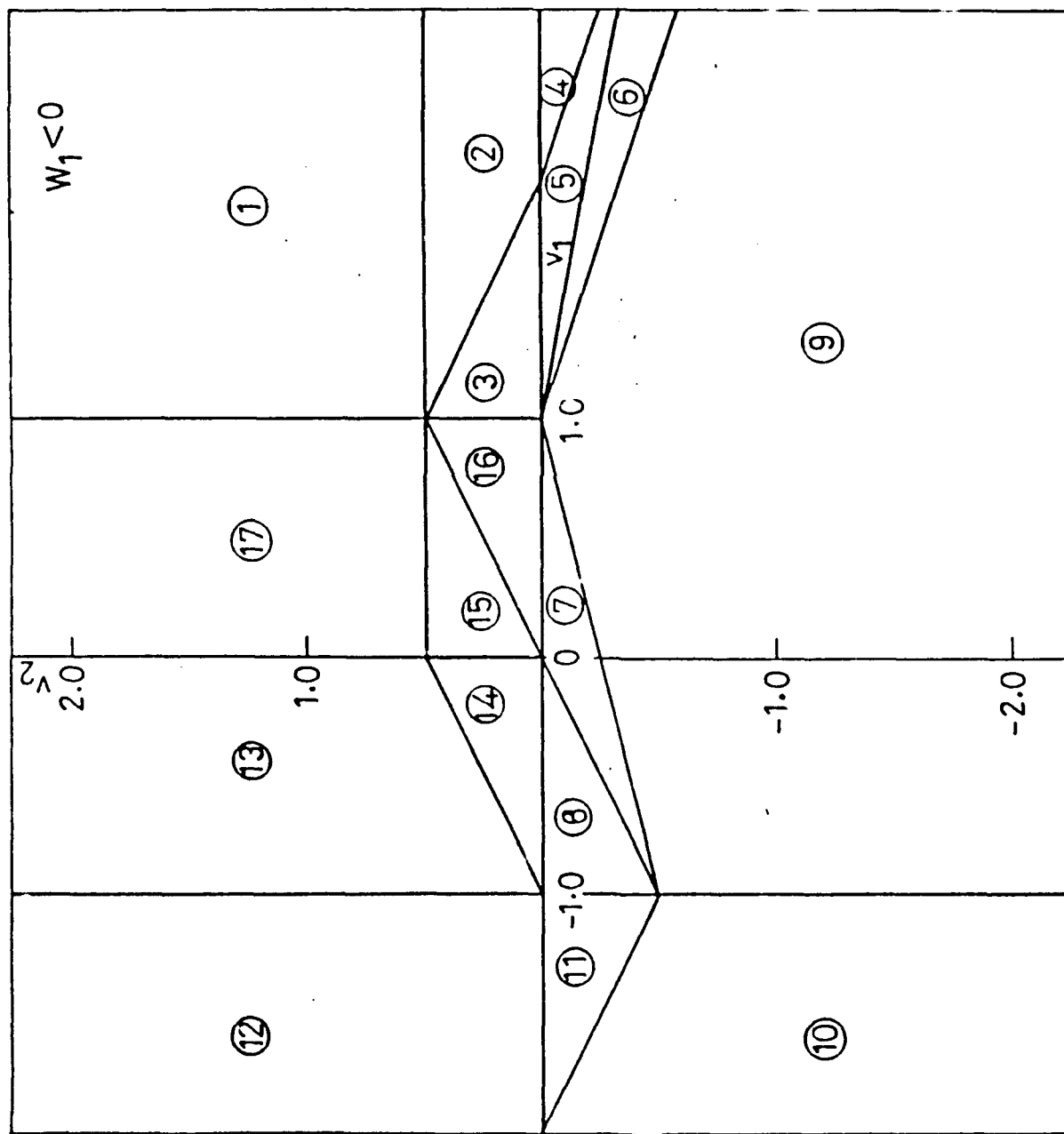
$$\bar{e}(A_3B^1) = E(A_3B^1)$$

$$\Rightarrow U_2 = 0$$

LOW ENERGY ORDERED STRUCTURE . ISO - ENERGY LINE







SUBLATTICE DIVISION METHOD

- ATOMIC SITES OF HCP STRUCTURE CAN BE DIVIDED INTO 6, 8, 10, 16, 20, 24 AND 28 SUBLATTICES
- SUBLATTICE / LAYER
- POPULATE LAYERS : ALL POSSIBLE A & B ATOMS
- STRUCTURES : STACKING OF LAYERS
- RELATIVE STABILITY OF STRUCTURES
- STABILITY DOMAINS
- COMPOSITE MAP

RESULTS : 15 STRUCTURES

A_5B , A_3B (3), A_2B (1), A_1B_5 , A_7B_5 ,
 AB (5)

CRYSTALLOGRAPHIC DETAILS :

BRAVAIS LATTICE

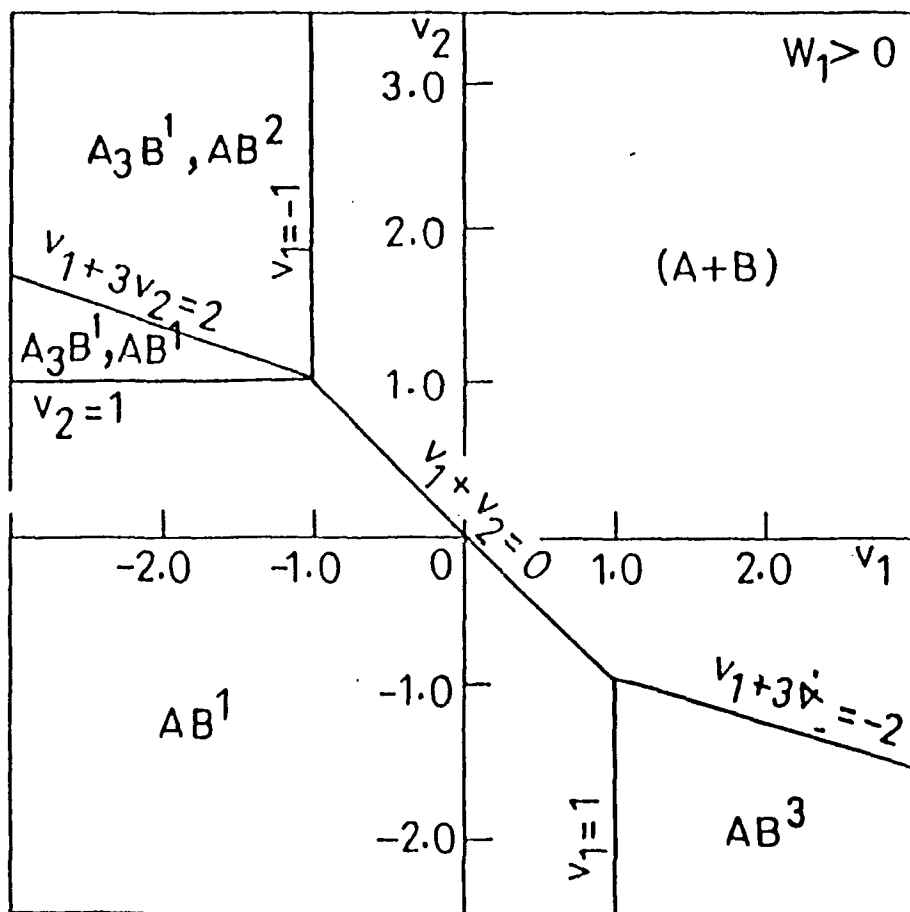
SPACE GROUP

NO OF ATOMS PER UNIT CELL

PEARSON SYMBOL

LATTICE PARAMETERS

COORDINATES OF EQUIVALENT POSITIONS



- RESULTS

-- SUBLATTICES 6, 8(2), 10, 12(2), 14(2),
16(2), 20, 24(2), 28(2)

FOR GROUND STATE 6, 8(2), 10, 12(2), 14(2)

- $W_1 < 0$

- 15 GROUND STATE STRUCTURES

A_5B , $A_3B(3)$, $A_2B(4)$, A_7B_5 , A_7B_5 , $AB(5)$

- $W_1 > 0$

4 GROUND STATE STRUCTURES OUT OF ABOVE
IS

-- DEGENERATE STRUCTURES

1. $A_5B(I)$

$A_5B(II)$

$A_5B(III)$

HEXAGONAL

ORTHORHOMIC

MONOCLINIC

2. A_7B

PARTIAL ORDERD

6 SUBLATTICES

ORDERED

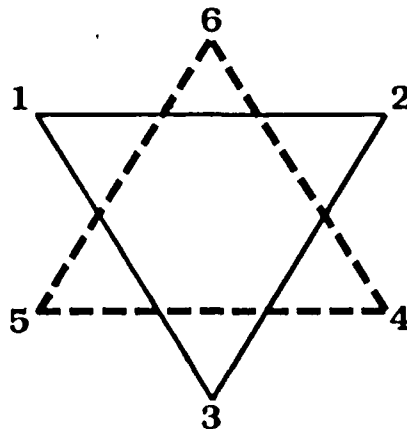
8 SUBLATTICES

-- SOLID SOLUTION

MISCIBILITY GAP

ADJACENT STOICHIOMETRIC STRUCTURES BASED ON
SAME SUBLATTICES (GROUND STATES PARTIALLY OCCUPIED)

CLUSTER METHOD



- **MOTIF**
- **CLUSTER**
- **WEIGHT**
- **ENERGY: Linear function of cluster concentration**
- **MINIMISATION OF ENERGY: Linear programming method (Two cluster solution)**
- **Realisation of solution on hcp atomic sites in a consistent manner**
- **RESULT : 9 structures**
 A_3B , $A_3B(3)$, A_2B , $AB(4)$
- **LIMITATIONS**

- CLUSTER METHOD

- MOTIF $X_k w_k = Y_k$ (WEIGHTED FRACTION)

- CLUSTER

13 POSSIBLE CLUSTES

- WEIGHT

$$Y_1 + Y_2 + Y_3 + Y_4 + Y_5 + Y_6 + Y_7 + Y_8 + Y_9 + Y_{10} + Y_{11} + Y_{12} + Y_{13} = 1 \quad (1)$$

$$Y_2 + 2Y_3 + 2Y_4 + 2Y_5 + 3Y_6 + 3Y_7 + 3Y_8 + 4Y_9 + 4Y_{10} + 4Y_{11} + 5Y_{12} + 6Y_{13} = 6C \quad (2)$$

- ONE CAN WRITE NO OF AB BOND (q_j) AS

$$\begin{aligned} \frac{q_j}{N} &= \frac{1}{2} \sum_k q_{jk} Y_k \quad \text{FOR } j = 1, 2 \\ &= \sum_k q_{jk} Y_k \quad \text{FOR } j = 3 \end{aligned}$$

- ONE CAN OBTAIN THE CONFIGURATIONAL ENERGY

$$\begin{aligned} E = \frac{1}{2} N W_1 [&Y_2 (1 + u_1 + u_2) + Y_3 (1 + 2u_1 + 2u_2) + Y_4 (2 + u_1 + 2u_2) \\ &+ Y_5 (2 + 2u_1) + Y_6 (3u_1 + 3u_2) + Y_7 (2 + u_1 + 3u_2) \\ &+ Y_8 (2 + 2u_1 + u_2) + Y_9 (2 + 2u_1) + Y_{10} (2 + u_1 + 2u_2) \\ &+ Y_{11} (1 + 2u_1 + 2u_2) + Y_{12} (1 + u_1 + u_2)] \end{aligned}$$

- SOLUTIONS : LINEAR PROGRAMMING
METHOD

RESULTS

$$W_1 < 0$$

$v_1 \geq -1$ $v_1 \geq 2v_2$ $v_2 \leq 0$	$A + A_3B^1$		AB^2	
$v_1 \geq 2v_2$ $0 \geq v_2 \geq 1/2$ $v_1 + 2v_2 \leq 2$	$A \rightarrow A_5B$	A_5B $A_3^+B^3$	AB^4	
$v_1 + 2v_2 \geq 2$ $v_2 \leq 1/2$	$A \rightarrow A_5B$	A_5B $A_3^+B^3$		
$v_1 \geq 1$ $v_2 \geq 1/2$	$A \rightarrow A_5B$	$A_5B \rightarrow A_2B^1$	$A_2B^1 \rightarrow AB^1$	
$v_1 = 1$ $v_2 \geq 1/2$	$A \rightarrow A_5B$		$A_2B^1 \rightarrow AB^3$	
$v_1 \leq 1$ $v_1 \leq 2v_2$ $2v_1 \leq v_2$	$A \rightarrow A_5B$			
$0 \leq v_1 \leq 1$ $2v_2 \geq v_1$	$A \rightarrow A_5B$	A_5B $A_3^+B^2$		
		1/6	1/4	1/3
		COMPOSITION (c)		
				1/2

Fig. 7. Different structures obtained by cluster method as a function of composition

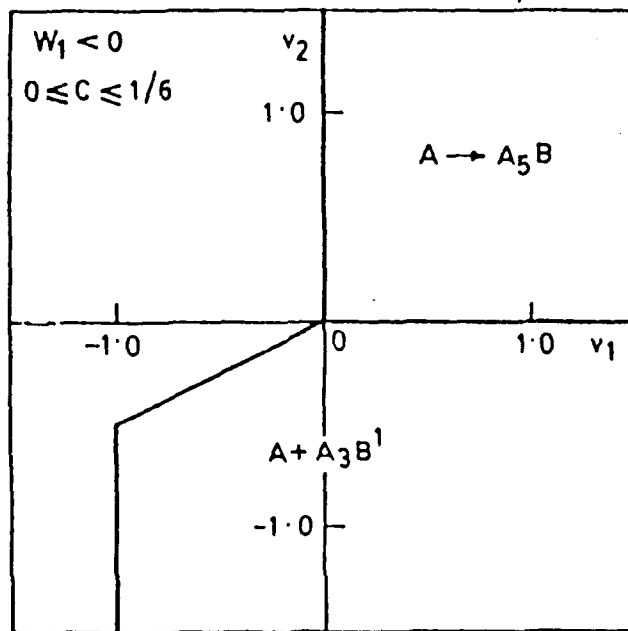
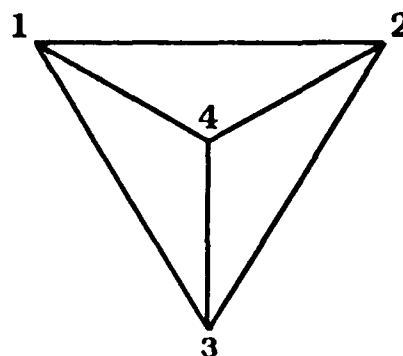
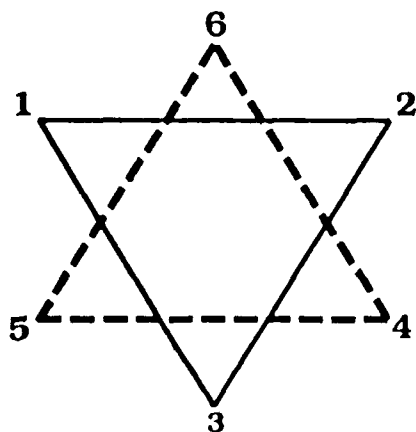


Fig. 3. Stability regions of structures obtained by cluster method as a function of interchange energy ratios v_1 and v_2 for $W_1 < 0$ and $0 \leq C \leq 1/6$. Arrows indicate stable solid solution at intermediate composition while the plus sign corresponds to a miscibility gap.

CONFIGURATION POLYHEDRON METHOD

- ➔ MOTIF
 - ➔ Structural inequalities:
half space (r_1, r_2, r_3, C)
 - ➔ Convex polyhedron: Configuration polyhedron
 - ➔ Realisation of solution on hcp atomic sites in a consistent manner
 - ➔ RESULTS
 - ➔ 15 structures
 - ➔ Series of long period APB modulated superstructures with stoichiometries $A_{n+3}B_{n+1}$
 - ➔ Entire surface of the configuration polyhedron corresponds to ground state structures
 - ➔ LIMITATIONS
-



CONFIGURATION POLYHEDRON METHOD

MOTIF

$$E/NW_1 = (3c - \frac{r_1}{N}) + (3c - \frac{r_2}{N})u_1 + (3c - \frac{r_3}{N})u_2$$

STRUCTURAL INEQUALITIES (M=14)

$$r_1, r_2, r_3, c$$

EACH INEQUALITY REPRESENTS A HALF SPACE BOUNDED BY A HYPERPLANE ON WHICH THE INEQUALITY BECOMES EQUALITY

SOLUTION : 4 INEQUALITIES FROM THE SET OF M ARE SELECTED AND TREATED EQUALITY
POSSIBILITIES (i) SOLUTION DOES NOT EXIST

(ii) A SOLUTION EXISTS BUT DOES NOT SATISFY ONE OR MORE REMAINING INEQUALITIES

(iii) A SOLUTION EXISTS THAT SATISFIES THE REMAINING INEQUALITIES

ONLY CASE (iii) CORRESPONDS TO A VERTEX OF CONFIGURATION POLYHEDRON

REALISATION OF STRUCTURE ON HCP ATOMIC SITES

RESULTS

LIMITATIONS (i) VIRTUAL STRUCTURE
(ii) STRUCTURAL REALISATION

One can write a general expression for the number r_1, r_2, r_3 of B-B bonds, concentration Y_1, Y_2, Y_3 , and energy of the n th member of the series as follows:

(18)

$$r_1 = \frac{3n(n+1)}{2(n+2)^2},$$

(19)

$$r_2 = 0,$$

(20)

$$r_3 = \frac{3(n+1)}{2(n+2)^2},$$

(21)

$$C_n = \frac{n+1}{2(n+2)},$$

(22)

$$Y_1 = \frac{1}{(n+2)^2},$$

(23)

$$Y_2 = \frac{3(n+1)}{2(n+2)^2},$$

(24)

$$Y_3 = \frac{n(n+1)}{(n+2)^2}$$

(25)

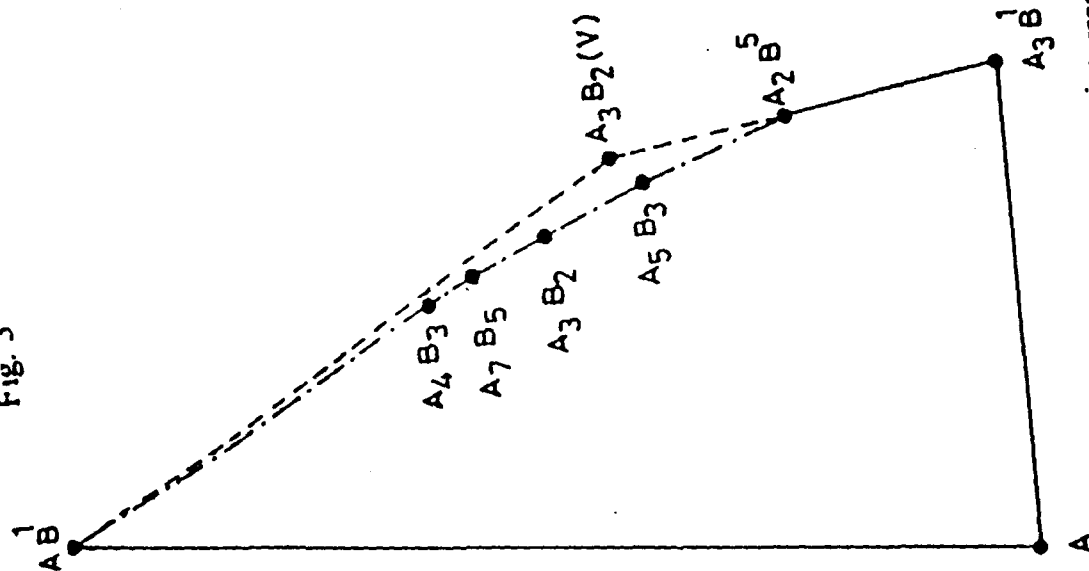
$$\frac{E_n}{NW_1} = \frac{3n+1}{2(n+2)^2} [2 + (n+2)v_1 + nv_2].$$

and

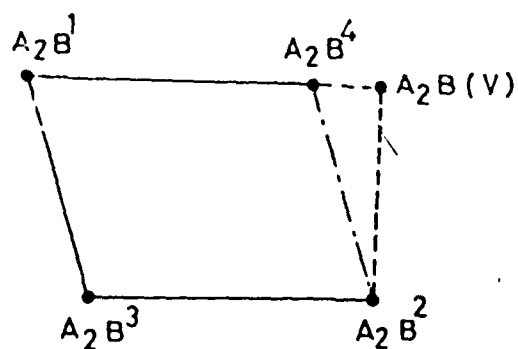
$$a = a_d [n+2] [100]$$

SPACE GROUP
P6₃/mmc

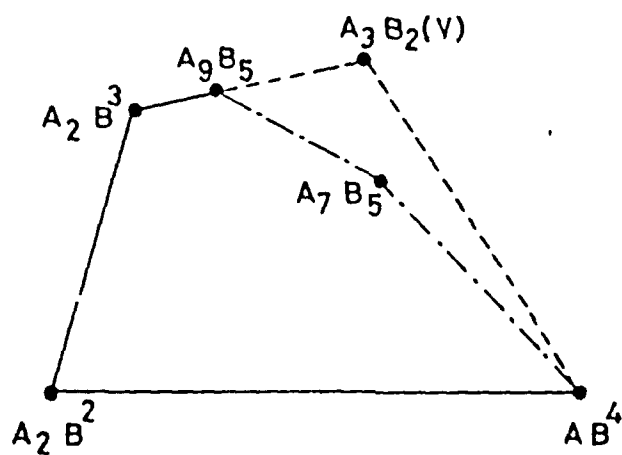
Fig. 3



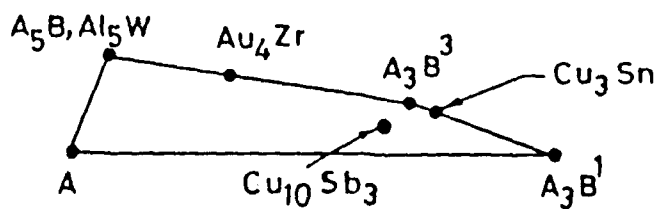
2D planar surface of configuration polyhedron obtained by intersection of hyperplanes 2 and 8. The solid lines join the vertices corresponding to real structures. The broken lines join the vertices which correspond to real and virtual structures while the chain lines join the points which correspond to the structures obtained by appropriate cluster combinations. The structures succeeding A_4B_3 ($n > 5$) are not shown in the figure, since the points corresponding to each structure are very close.



(a)



(b)



(c)

2D planar surface of configuration polyhedron obtained by intersection of hyperplanes (a) 4 and 5, (b) 5 and 9 and (c) 1 and 2.

MULTI-ATOM INTERACTION METHOD

- ➔ **CLUSTER METHOD**
- ➔ **MOTIF [Tetrahedron]**
- ➔ **Multi-atom interaction parameters
[4 body force]**
- ➔ **Look for minimum number of variables**
- ➔ **MINIMISE ENERGY IN PARAMETER SPACE**
- ➔ **RESULTS**

A_3B , A_2B , AB , AB_2 and AB_3

Table 1. Possible cluster configurations on the motif (Fig. 1) and their energies.

cluster type	cluster configuration/ sites occupied by B atoms	weight of the cluster	composition of the cluster	first neighbour unlike pairs	second neighbour unlike pairs	cluster energy
i		w_i	c_i	n_i'	n_i''	ϵ_i
0	-	1	0	0	0	0
1	1	3	1/4	2	1	$3/2W(1+\alpha)$
2	4	1	1/4	0	3	$3/2W(1+\beta)$
3	1,2	3	1/2	2	2	$2W$
4	1,4	3	1/2	2	2	$2W$
5	1,2,3	1	3/4	0	3	$3/2W(1+\gamma)$
6	1,2,4	3	3/4	2	1	$3/2W(1+\delta)$
7	1,2,3,4	1	1	0	0	0

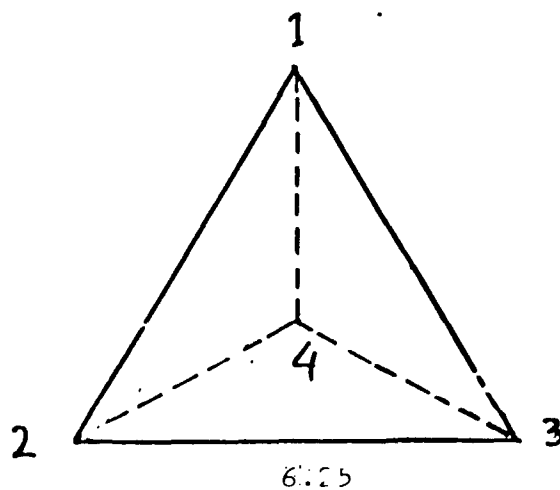
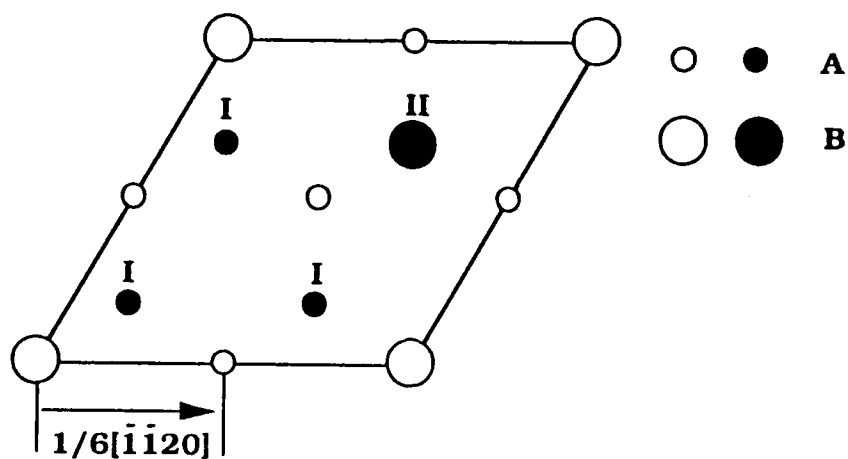


Table 3. Crystallographic data for the structures pertinent to the ground state ordered h.c.p. alloys.

Phase	Space group	Pearson symbol	Lattice vector in units of a_a and c_a			M/K	Sublattice type occupied by B atoms
			a	b	c		
$A_5B(I)$	$P6_3/m$	hP6	[210]	[110]	[001]	6	1
	D_{3h}^{13}					2	
$A_5B(II)$	$Pnmm(Pnmm)$	oP12	[110]	[330]	[001]	12	1,9
	D_{2h}^{13}					2	
$A_5B(III)$	Pm	mP12	[120]	[220]	[001]	12	1,9
	C_2^1					3	
A_5B^1	$P6_3/mmc$	hP8	[200]	[020]	[001]	8	1,5
	D_{6h}^4					3	
$A_5B^2(I)$	$C2mm(Amm2)$	oC16	[420]	[020]	[001]	8	1,6
	C_{2v}^{14}					3	
$A_5B^2(II)$	Pm	mP8	[110]	[220]	[001]	8	1,5
	C_2^1					2	
A_5B^3	$Pnmm(Pnmm)$	oP8	[210]	[020]	[001]	8	1,6
	D_{2h}^{11}					3	
A_2B^1	$P6_3/m$	hP6	[210]	[110]	[001]	6	1,2
	D_{3h}^1					2	
A_2B^2	$Ccmm(Cmcm)$	oC12	[120]	[300]	[001]	6	1,4
	D_{2h}^{17}					2	
$A_2B^3(I)$	$Pn2_1m(Pmn2_1)$	oP12	[110]	[330]	[001]	12	1,2,9,10
	C_{2v}^7					2	
$A_2B_3(II)$	$Ccmm(Cmcm)$	oC12	[330]	[110]	[001]	12	1,4,9,12
	D_{2h}^{17}					3	
$A_2B^4(I)$	$Pnmm(Pnmm)$	oP12	[110]	[330]	[001]	12	1,3,5,1
	D_{2h}^{13}					2	
$A_2B^4(II)$	Pm	mP12	[120]	[220]	[001]	12	1,3,9,11
	C_2^1					3	
A_9B_5	Pm	mP14	[310]	[230]	[001]	14	1,2,3,5,11
	C_2^1					3	
A_7B_5	Pm	mP12	[120]	[220]	[001]	12	1,2,4,9,12
	C_2^1					3	
AB^1	$P6_3/m2$	hP2	[100]	[010]	[001]	8	1,2,3,4
	D_{3h}^1					3	
AB^2	$Pcmm(Pmma)$	oP4	[210]	[010]	[001]	8	1,2,5,6
	D_{2h}^2					3	
AB^3	$Pnmm(Pnmm)$	oP4	[210]	[010]	[001]	8	1,2,7,8
	D_{2h}^{13}					3	
AB^4	$Pnam(Pnma)$	oP8	[110]	[220]	[001]	8	1,2,6,7
	D_{2h}^{10}					2	
AB^5	$Pcam(Pbcm)$	oP8	[110]	[220]	[001]	8	1,2,5,8
	D_{2h}^{11}					2	

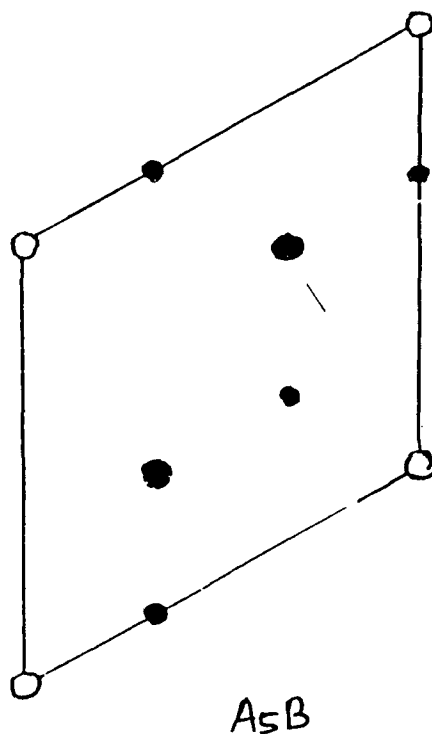


SPACE GROUP : $P6_3/mmc$

NO OF ATOMS PER : 8

UNIT CELL

PEARSON'S SYMBOL : $hP8$



$$E_{AsB} = \frac{1}{2} (1 + v_1 + v_2)$$

AsB : HEXAGONAL

$P\bar{6}2m$ OR D_{3h}^3 ; 6 ATOMS PER UNIT CELL

$hP6$

$a = a_d[210]$, $b = a_d[\bar{1}10]$ and $c = c_d[001]$
co-ordinates of equivalent positions

- (1) 1 B atom at $(0, 0, 0)$ ($\bar{6}2m$)
- (2) 2 A atoms at $(\frac{1}{3}, \frac{2}{3}, 0)$; $(\frac{2}{3}, \frac{1}{3}, 0)$ ($\bar{6}$)
- (3) 3 A atoms at $(\frac{1}{3}, 0, \frac{1}{2})$; $(0, \frac{1}{3}, \frac{1}{2})$; $(\frac{\bar{1}}{3}, \frac{\bar{1}}{3}, \frac{1}{2})$ ($m\bar{2}c_2$)

STABILITY OF OBSERVED HCP SUPERSTRUCTURE

Ti_3Al , Mn_3Sn , Mg_3Cd
(D019)

A_3B^1

WC & $LiRh$

AB^1

$MgCd$

AB^2

Cu_3Sn

- E(TWO PHASE MIXTURE of
 $A_3B^1 + A_3B^3$)

Sb_3Cu_{10}

- E(TWO PHASE MIXTURE
 $A + A_3B^3$)
OK

E(POLY PHASE MIXTURE
 $A_5B + A_3B^1 + A_3B^3$)

$ZrAu_4$

- L($A_5B + A_3B^3$)

Al_5W

- L(A_5B)

STABILITY OF EXPERIMENTALLY OBSERVED HCP SUPERSTRUCTURES

A_3B^1 :	Ni ₃ Sn, Mg ₃ Cd, Ti ₃ Al	$W_1 < 0, v_1 > -1, v_2 < 0$
A_2B^2 :	Pt ₂ Ta	$W_1 < 0, 0 < v_1 < 1, v_2 < 0, v_1 - v_2 > 0$
AB^1 :	WC, LiRh	$W_1 < 0, v_1 > -1, v_2 > 1/2$
AB^2 :	MgCd	$W_1 < 0, v_1 > -1, v_2 < 0$
$A_5B + A_3B^3$:	Au ₄ Zr	$W_1 < 0, v_1 > 1, 0 < v_2 < 1$
$A_3B^1 + A_3B^3$:	Cu ₃ Sn	$W_1 < 0, v_1 > 0, v_2 = 0$
$A + A_5B + A_3B^1 + A_3B^3$:	Cu ₁₀ Sb ₃	$W_1 < 0, v_1 > 0, v_2 > 0$

7. Stability

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STABILITY

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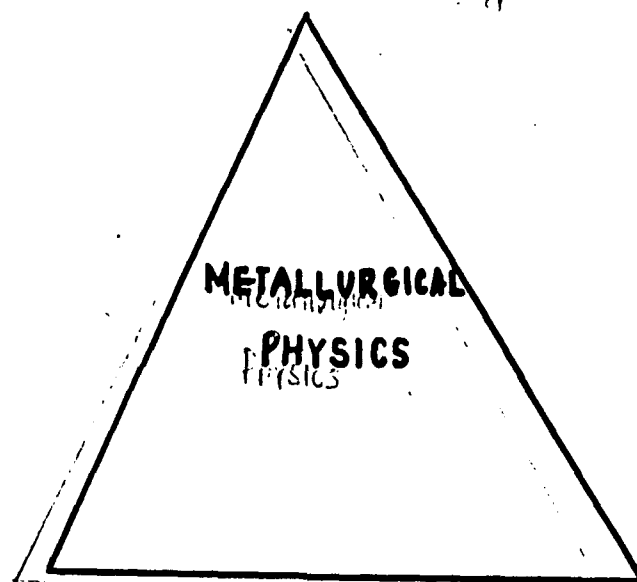
STABILITY OF INTERMETALLICS

A Metallurgical Physics Perspective

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PHYSICAL
PHYSICAL METALLURGY
EMPIRICAL EXPLANATION OF ALLOYING



CONDENSED
MATTER
PHYSICS

SOLID
STATE
CHEMISTRY

QUANTUM THEORY OF
STRUCTURE &
BONDING

Electronegativity
Valence

DOES THIS ALLOYING MODEL VALID?

No

Tight binding, DFT

Protagonists

Pettifor, Williams,
Watson & Bennett?



Such basic splitting
is not warranted for
transition metal
Cohesion

Better numerical
agreement

Acceptable

Pseudopotential
theorists

Chelikowsky & Phillips,

Hafner?

Alonso & Girifalco

Hodges & Stott



s , ϕ , have well
defined quantum
physical status,

Rather poor
agreement

STRUCTURAL STABILITY

FIRST PRINCIPLES
APPROACH



UNDERSTANDING
ALLOYING

THEORY/MODEL FOR
COHESION

EMPIRICAL
SCHEMES



PREDICTION

STRUCTURAL
SYSTEMATICS

SEMIEMPIRICAL METHODS

- Establish the trend using appropriate alloy theory parameters
- Setup a microscopic model in terms of these parameters.
- Pseudopotential & Tight binding methods
- Pair potential analysis (Machlin)
- Macroscopic Atom model
(Miedema)
- Interstitial electron density model (Schubert, Johnson)

PAIR POTENTIALS

$$E = \frac{1}{2} (N) \sum_{R_{ij} \neq 0} \phi(R_{ij})$$

- Absence of volume dependence
- Ordering Energy may be represented

$$E = F(\rho) + \frac{1}{2} \sum \phi(R)$$

Volume dependence
(structural term)

EMBEDDED ATOM MODEL

MIEDEMA'S MODEL

ALLOY $\equiv$ ASSEMBLY OF
NEUTRAL W-S CELLS

PARAMETERS :

- electron density (ρ ; $\rho^{1/3}$)
- Chemical potential due to electronic charge (ϕ^*)
- Molar volume

$$\Delta^{\circ}H_f \equiv \left\{ -P(\Delta\phi^*)^2 + Q(\Delta\rho^{1/3})^2 \pm R \right\} \\ \times f(c)$$

MIEDEMA MAPS

$$\langle \Delta\phi^*, \Delta\rho^{Y_B} \rangle$$

$U_d = \text{No. of } d \text{ electrons} \times \text{energy of } d \text{ electron}$

$$U_d = \int_0^{E_F} N(E) dE \cdot E - N_d E_d^{\text{at}}$$

$$= - \frac{W_d}{20} (10 - N_d) N_d \quad \text{FRIEDEL}$$

W_d : width of d-band

N_d : No. of d-electrons

For an $A_x B_{1-x}$ alloy

$$x = 1/2$$

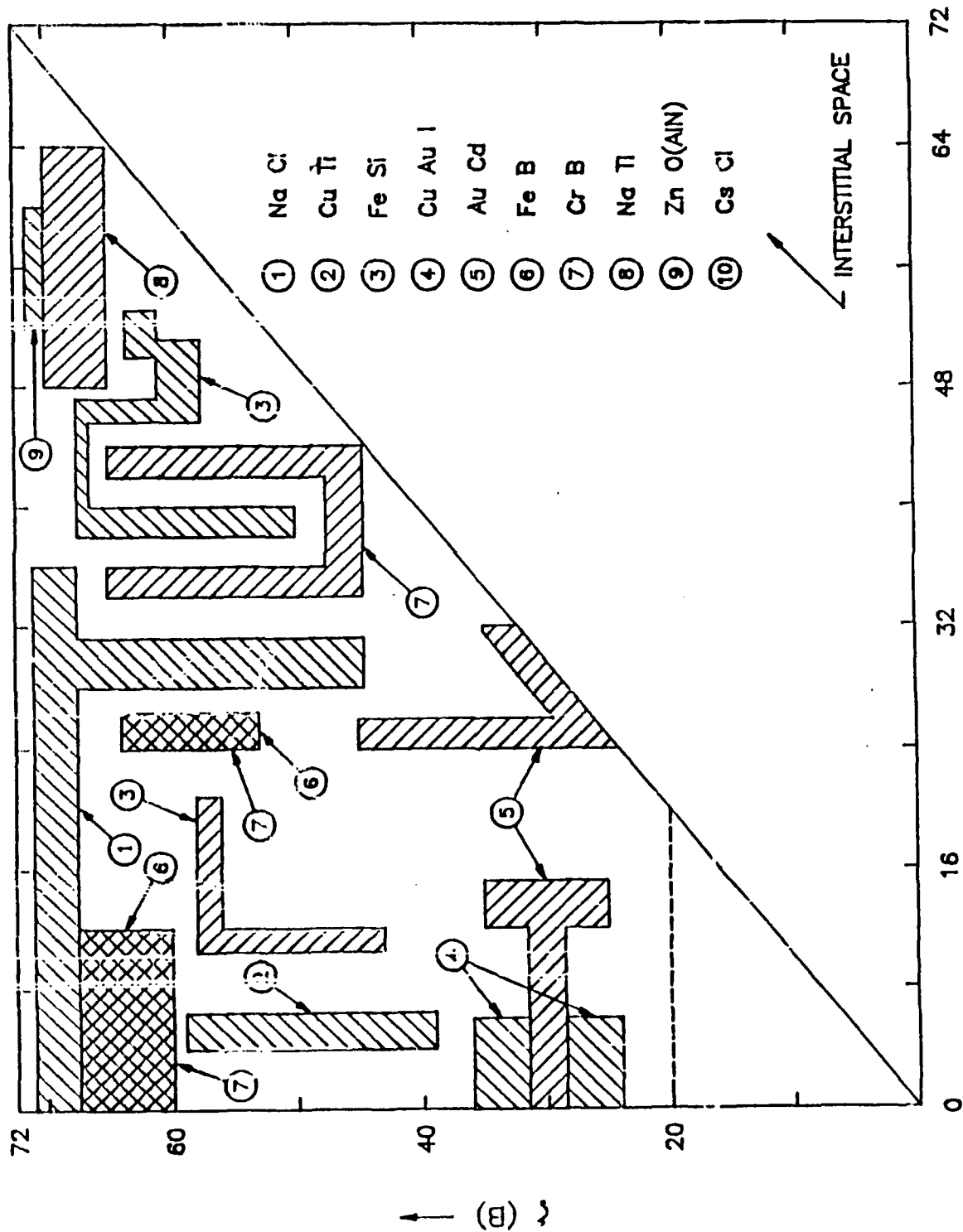
$$\int_0^{E_F} E N(E) dE - 1/2 \int_0^{E_F^A} E N(E) dE - 1/2 \int_0^{E_F^B} E N(E) dE$$

$$= - \frac{W_{AB}}{20} \bar{n} (10 - \bar{n}) + \frac{W_A}{40} n_A (10 - n_A) + \frac{W_B}{40} n_B (10 - n_B) - 1/4 \Delta \delta n$$

$$\bar{n} = (n_A + n_B)/2$$

$$\delta n = n_A - n_B$$

PETTIFOR'S
MODEL



$\xi (A) \longrightarrow$
7.11

Fig. 2

THE QUANTUM character of the chemical elements is reflected directly in the periodic table. This two-dimensional arrangement of the elements is a consequence of Schrödinger's equation. Each element in the periodic table is characterised by two co-ordinates, namely its period and group. To classify the structures of binary compounds, I have reduced this to a single co-ordinate, as described in the main text by arranging the elements along a one-dimensional axis, their relative ordering being given by what I have called the Mendeleev number.

The arrangement of the periodic table shown here is slightly different from usual (*New Scientist*, 7 March 1985, p 32). This arrangement places the group IIA elements beryllium and magnesium with group IIB and separates the divalent rare earths or lanthanides (those that have two valence electrons) from the trivalent. The way I have ordered the elements in group IVA reflects the so-called lanthanide contraction: hafnium has a smaller core size than zirconium. My arrangement of group V leads to a marginally better separation of structures of compounds than running the string straight from nickel to platinum. The anomalous ordering of gallium with respect to alu-

2: Stringing up the periodic table

minium arises because gallium has a full core of *d* electrons. Chemists well know that the second row elements boron, carbon, nitrogen, oxygen and fluorine behave differently from the other elements in their respective groups. They are much more electronegative due to the absence of *p* electrons in the core. □

The string running through this modified periodic table puts all the elements in sequential order, given by the Mendeleev number

Typically What do the Material Scientists want from systematization studies?

- Under What conditions do two elements A & B Combine and if so
- Do they form compounds or Solid / liquid Solutions?

More Specifically they look for

- | | |
|--|---|
| • Number of compounds | • Extent of solid solubility |
| • Crystal Structure information | • Type of solid Solubility |
| • Stability of compounds
(polymorphic & other transition,
cohesive energy, Lattice Stability
Parameters etc.) | isomorphous
Eutectic
peritectic & a host
of others |

- If they are insoluble then Why?

- Basically, these are the primary information, which together form a comprehensive physical Metallurgical data base. No doubt, one can take other properties like

- thermodynamic
- electrical, magnetic
- transport properties

but in my opinion they do not form a simple & minimal basis.

• CRITICAL APPRAISAL

- In its core the model is empirical.
- Subtle effects like magnetic contribution to stability is neglected
- Alloys with Si, Ge etc are not satisfactorily represented.
- The physics of alloying as advanced by this model is strictly incorrect, although its numerical agreement with precise first principle calculations is surprisingly good.

• APPLICATIONS

- Extrapolation/ Interpolation for limited ΔH_f data bank.
- Calculation of interfacial energies
- Prediction of glass formation ranges
- Assessing the relative stability trends
- Analysing solid solubility data

* USE OF BASIC COORDINATES TO CRYSTAL STRUCTURE SYSTEMATICS

- An algorithm to generate probable structural alternatives

- Structure maps
- Simple phenomenological correlations
- A truly first principles approach is a non starter by itself

- Effect of various approximations on the output !

• Is there a UNIVERSAL THEORY?

SIMPLE METAL
ALLOYS

- Pseudo potential

TRANSITION
METAL ALLOYS

- Tight binding
- LMT0(ASA)

HYBRID
VARIETIES

DFT (LDA); ?
ASW

STABILITY ?

$$F = -\beta^{-1} \ln Z \quad 1$$

$$Z = \text{Tr} \{ \exp (-\beta H) \} \quad 2$$

$$\beta = 1/k_B T$$

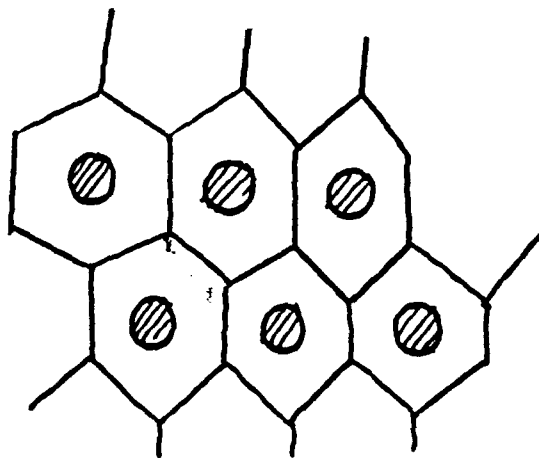
$Z =$ Partition function

$H =$ a (ground state) energy function

$$H = \sum H_{e-e} + H_{i-i} + H_{i-e}$$

$$H = E_k + E_p \quad (\text{Schrödinger equation, Virial theorem, } \dots)$$

SIMPLE METAL ALLOYS



METAL = SCREENED + DELOCALIZED
ION CORE CONDUCTION
ELECTRONS

$$\Delta^{\circ} H_f = x \Delta \bar{H}_A + (1-x) \Delta \bar{H}_B$$

$$\Delta^{\circ} \bar{H}_A = (E_A - E_A^{\circ})$$

$$E = E(r_s)$$

r_s = volume/electron , electron density

$$E = \underbrace{\sum E_k + E_{el} + E_{ex} + E_c}_{E_{eg}} + U_{Pot.} + U_{Madelung}$$

$$E = E_{eg} + \text{Structure dependent contribution.}$$

Depending on the sophistication, plug in appropriate E_i

$$\left. \frac{dE}{dr_s} \right|_{r=r_s}, \quad \frac{\partial^2 E}{\partial r_s^2}, \quad \text{give equilibrium conditions.}$$

For a binary $A_x B_{1-x}$ the final expression

$$E (\text{Per atom}) = Z^* \left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s} - 0.115 + 0.031 \ln r_s \right) + \frac{1}{4/3 \pi r_s^3} [x \mu_A + (1-x) \mu_B] - \frac{\alpha}{r_s} Z^{*5/3}$$

$$Z^* = x Z_A + (1-x) Z_B$$

$$\alpha = 1.792 \text{ (fcc)}$$

$$\mu_\alpha = 2\pi e^2 Z_\alpha (r_c^\alpha)^2$$

$$\Delta F_{mix} = \Delta E_{mix} - T \Delta S_{mix}$$

The present study attempts to devise a single coordinate structure map.

Why one parameter?

Periodic table has one dimension, namely Z

Is it possible by just providing one extra parameter to correctly account for the bonding trend?

Secondly is it possible to combine a few other independent parameters to get a single one which ~~has~~ is a compromise of competing tendencies?

Ans (i). Yes - one parameter

(ii) No - not truly independent

PRESENT PARAMETER

$$\chi \equiv \frac{\phi^*}{n_{ws} \cdot V} = \text{Volt/electrons}$$

• $\phi^* =$ Work function related electronegativity ($\propto E_F$)

$n_{ws} =$ electron density at W-S cell surface

$V =$ Volume/mole ...

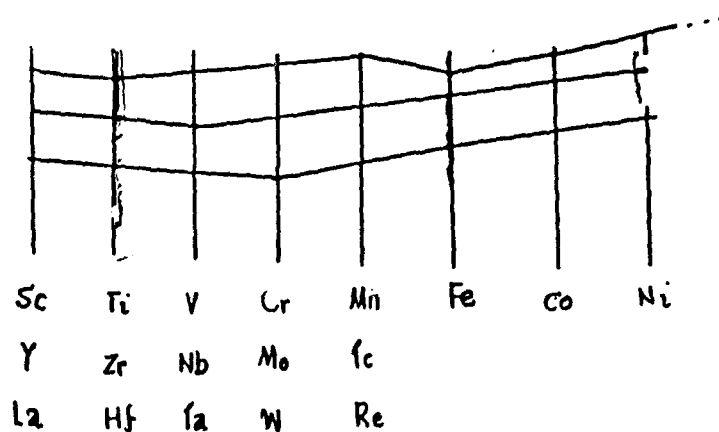
χ AS A STRUCTURE MAP PARAMETER

- Prediction of Solid Solubility
- Prediction of compound formation
- AB Structure type sorting
- The range of χ is increased by artificially stringing it in the decreasing order.

Ce : 1
H : 72 (actinide omitted)

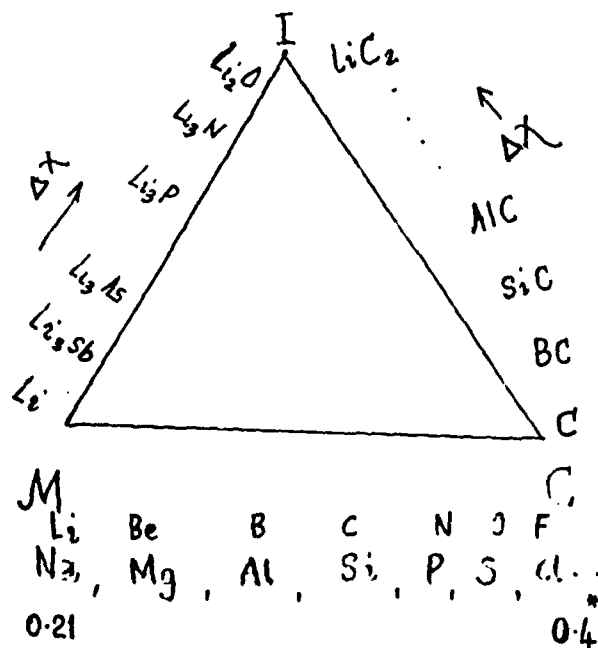
- Predicts reasonably solid solution exclusion and compound formation exclusion zone.
- Sort AB structure type only as good as any other single coordinate Map.

- The χ VARIATION FOR TRANSITION METAL PERIODS IS RATHER IRREGULAR



- Also there is a drop in χ in going from IA $\rightarrow$ IIA
 ie. Li $\rightarrow$ Be : Na $\rightarrow$ Mg etc.
 $1s^1 - 1s^2$ $2s^1 - 2s^2$
- χ does not appear to be a smooth function of Z .
- $\chi \neq$ Electronegativity ?
 $\equiv$ an energy parameter, characteristic of the Condensed state, not the elemental state
 $\therefore$ It may not therefore obey the trends of an atomic coordinate.

- If we propose χ as measure of electronegativity then the high electronegative elements on the extreme right has no option other than Covalent bond.
- Low χ values of metals indicates that electron redistribution is rather easy upon homopolar bond formation. Low electronegativity suggests that transfer and delocalization of atomic valence shell into conduction band is ~~an~~ energy inexpensive



- 'Position' of H_2 requires reshuffling?

RELEVANCE OF χ W.R.T. PERIODIC TABLE

- χ decreases down the group, (save for Si-Ge) for s, p elements

Down the Group, the size (at. radii) increases,
and s, p, d levels in the solid state converge.
~ difference in $E_p - E_d$ comes down.

~ increased delocalization

~ increased metallicity

χ value decreases ~

If $\chi \approx$ av. one e^- energy of valence shell
then this trend is accepted.

- Slight upward shift in Si $\rightarrow$ Ge

Si: p block element - no d-band

Ge - imperfect Screening by d-band of the
valence s and p. As a net result there is
a slight d-band contribution $\rightarrow$ Shifting it to
Semiconductivity.

- Compared to Si, Ge has a lower band gap, (and high χ)

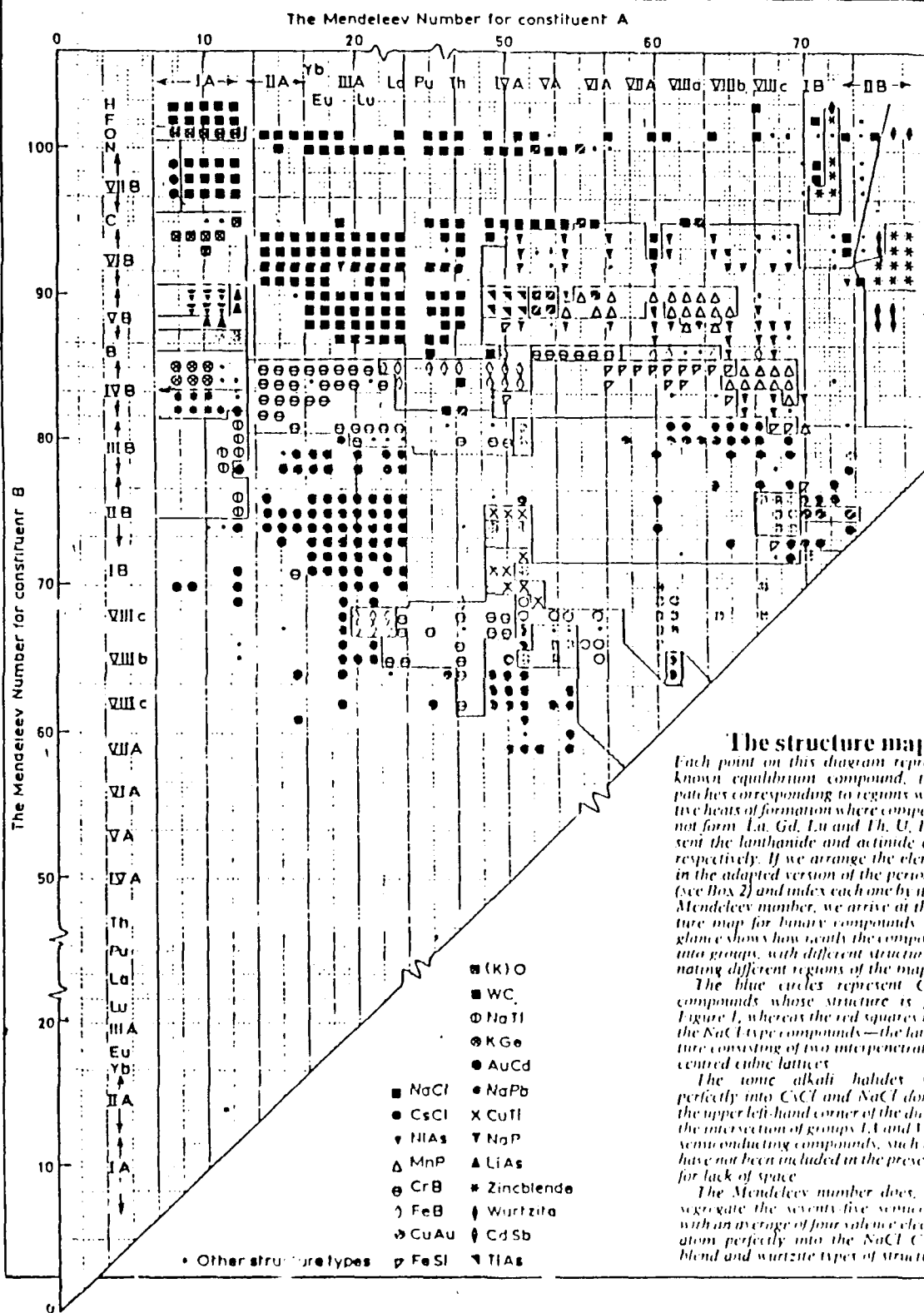
72 H 0.9106																
69 Li 0.2328	68 Be 0.2218															
66 Na 0.2059	51 Mg 0.1538															
63 K 0.17953	38 Ca 0.12919	27 Sc 0.1057	25 Ti 0.102256	32 V 0.11522	35 Cr 0.124167	47 Mn 0.14509	36 Fe 0.12343	46 Co 0.14227	49 Ni 0.1499	65 Cu 0.1913	64 Zn 0.19447	52 Ga 0.15425	70 C 0.34485	71 N 0.37283		
61 Rb 0.17338	34 Sr 0.11935	16 Y 0.09834	7 Zr 0.08788	2 Nb 0.084111	11 Mo 0.08933	26 Tc 0.1035	29 Ru 0.10771	33 Rh 0.11931	41 Pd 0.1317	59 Ag 0.18164	58 Cd 0.1833	53 In 0.15477	43 Sn 0.1335	39 Sb 0.12973		
60 Cs 0.1893	31 Ba 0.11462	4 La 0.087928	8 Hf 0.08793	5 Ta 0.08818	3 W 0.0946	18 Re 0.09276	24 Os 0.1009	28 Ir 0.10635	30 Pt 0.11004	40 Au 0.13181	55 Hg 0.15649	56 Tl 0.181147	50 Pb 0.14745	45 Bi 0.13782		

* ξ SCALE FOR 72 ELEMENTS

ξ $\frac{V}{\lambda}$ — ELEMENT SYMBOL

RARE EARTHS

1 Ce 0.0842	9 Pr 0.0889	12 Nd 0.08969	10 Pm 0.0891	13 Sm 0.0903	14 Eu 0.09046	15 Gd 0.0983	17 Tb 0.09151	19 Dy 0.09305	21 Ho 0.09453	20 Er 0.09183	22 Tm 0.09547	23 Yb 0.0963	Lu 0.095032
0 Ce 0.12668	+3				0. +2 Eu 0.12668							0. +2 Yb 0.13323	



The structure map

Each point on this diagram represents a known equilibrium compound, the bare patches corresponding to regions where compounds do not form. La, Gd, Lu and Th, U, Pu represent the lanthanide and actinide elements respectively. If we arrange the elements as in the adapted version of the periodic table (see Box 2) and index each one by its unique Mendeleev number, we arrive at this structure map for binary compounds. A quick glance shows how readily the compounds fall into groups, with different structures dominating different regions of the map.

The blue circles represent CsCl-type compounds whose structure is given in Figure 1, whereas the red squares represent the NaCl-type compounds—the latter structure consisting of two interpenetrating face-centred cubic lattices.

The ionic alkali halides segregate perfectly into CsCl and NaCl domains at the upper left-hand corner of the diagram, at the intersection of groups IA and VIIB. The semiconducting compounds, such as GaAs, have not been included in the present figure, for lack of space.

The Mendeleev number does, however, segregate the seventy-five semiconductors with an average of four valence electrons per atom perfectly into the NaCl, CsCl, zinc blende and wurtzite types of structure.

PRELIMINARY CONCLUSIONS ABOUT χ

- For s, p elements, the metallic state valence orbitals retain a large portion of atomic character and therefore χ exhibits a trend, coinciding with an atomic electronegativity

- The more the 's' orbitals are involved in bonding the larger is the χ . This is evidenced by $\chi_{Li} > \chi_{Be}$ etc..

$$\chi_{Na} > \chi_{Mg}$$

- Transition Metals exhibit a low range of $\Delta\chi$, besides having low χ themselves.

- Rare earths tend to group, mingle with the d-transition metals, thus unifying the general metallicity of these group. Note, the

Present form of periodic table tends to

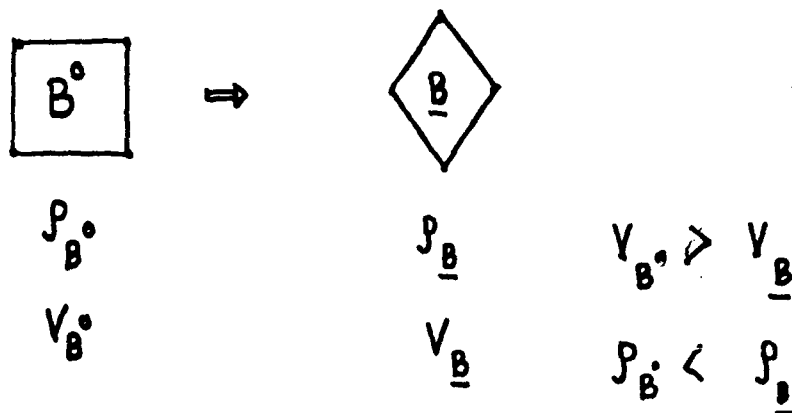
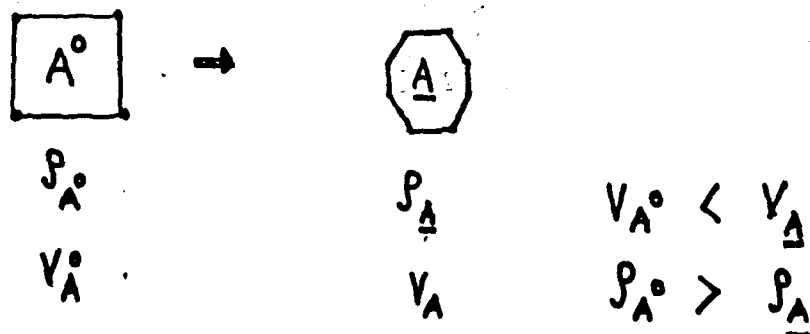
muddle this trend. i.e., After La,

La $\rightarrow$ Lu must be followed: But we write

La - Hf - Ta - W ... etc..

BASIC STEPS

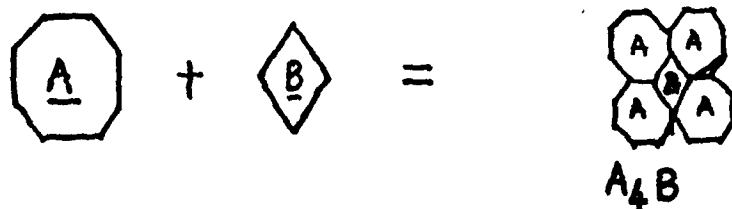
CELL PREPARATION



CELL PREPARATION : VOLUME EFFECT
STEP

Generates repulsive forces

CHARGE TRANSFER STEP



THIS IS ATTRACTIVE AS CHARGE
TRANSFER. DRIVEN BY CHEMICAL POTENTIAL
GRADIENT. ($\Delta\phi^*$)

ELECTROCHEMICAL FACTOR.

THUS ρ , ϕ COULD BE BASIC ALLOY THEORY
PARAMETERS.

BESIDES, THEY ARE CONNECTED TO ΔH_f .

ELECTRON DENSITY

$$\rho \text{ or } n = (V/Z)^{-1}$$

$$\frac{4}{3} \pi r_s^3 = V/Z$$

$$r_s = r_s/a_0$$

- Z Cannot be solved exactly in 3-D
- H is a composite term, again exact Calculations are impossible
- Approximations at this very basic level
 - Adiabatic approximation
 - one electron approximation
 - Self consistent treatments of e-e
(Various band structure models, DFT, PPT)
EMA, Molecular dynamics, cluster calculations)
- Incorporation of temperature effects
 - harmonic, quasi harmonic models
 - inadequate portrayal of lower T regime
- Computational accuracy

$$< \text{lev } \left(\frac{25 \text{ kCal}}{100 \text{ kJ/g.atom}} \right)$$

REQUIRED INPUT

- Set of Z_i
- eqm. spacing (Vegard's Law: Zen's Law)
- Core size, Madelung Constant

OUTPUT

FORMATION ENTHALPY.

ELECTRONEGATIVITY

BULK MODULUS (?)

SFE, APBE (?)

ORDERING ENERGY

VALIDITY

ONLY s, p ALLOYS

ATTRACTION

SIMPLE, ALLOWS EASY BREAK UP

INPUT

$W_i, \eta_i (i = A, B); W_{AB},$

SIMPLE ;

NO STRUCTURE DEPENDENCE

ABSENCE OF REPULSION TERM

BUT EXPERIMENTAL AGREEMENT

GOOD ?

How ?

How to incorporate structure ?

STRATEGY

(i) $N(E) \rightarrow$ density of states, structure sensitive.

(ii) FORCE THEOREM

Consider C Covalent sp^3 / tetrahedral

Si }
Ge } tetrahedral SC

↓ Ω

Sn - white tin, SC, tetragonal lower χ ,

Pb - FCC, metal, lower χ

Further

Al	Si	P	$\chi_{Si} = \frac{\chi_{Al} + \chi_P}{2}$
Ga	Ge	As	$\chi_{Ge} = \frac{\chi_{As} + \chi_{Ga}}{2}$
In	Sn	Sb	$\chi_{Sn} = \frac{\chi_{In} + \chi_{Sb}}{2}$

AlP

GaAs are also semiconducting.

InSb

As we go from Left $\rightarrow$ right in the periodic table

We move from

Metallic $\rightarrow$ Covalent binding

Li,	B, C, N, P, As.
Be, Ba	O ₂ , F ₂ etc...
etc..	

$\chi \longrightarrow$

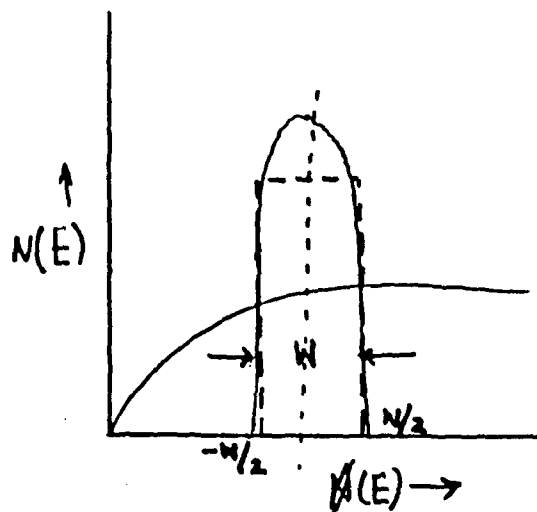
What is special about transition metals ?

- d electrons - spatially localized
- Covalent interaction
- Strongly bound to the core

TIGHT BINDING SCHEME

$$E = \underbrace{u_{\text{att}} + u_{\text{rep}}}_{u_d + u_{s-d} + u_{\text{others}}}$$

RECTANGULAR
BAND ASSUMPTION



TRANSITION METAL COHESION

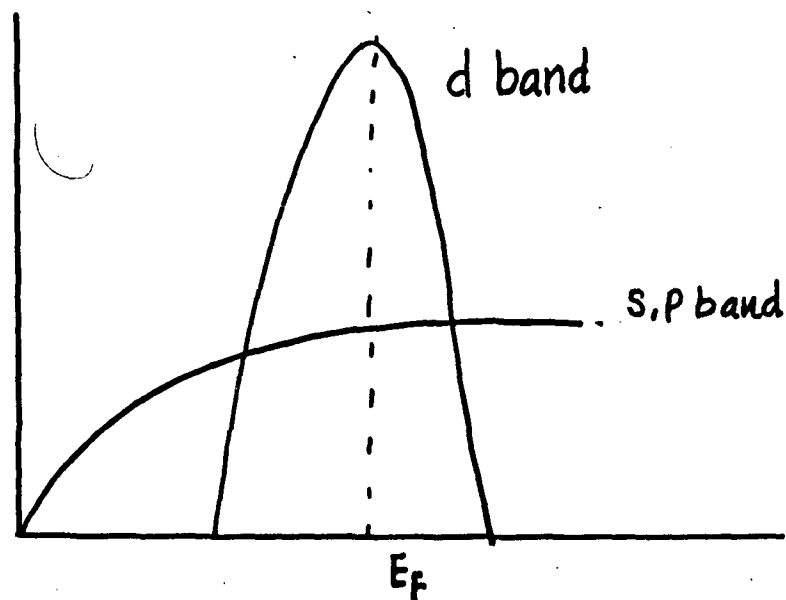
$$E = E_d + E_{s.p} + E_{s+d} + \text{others}$$

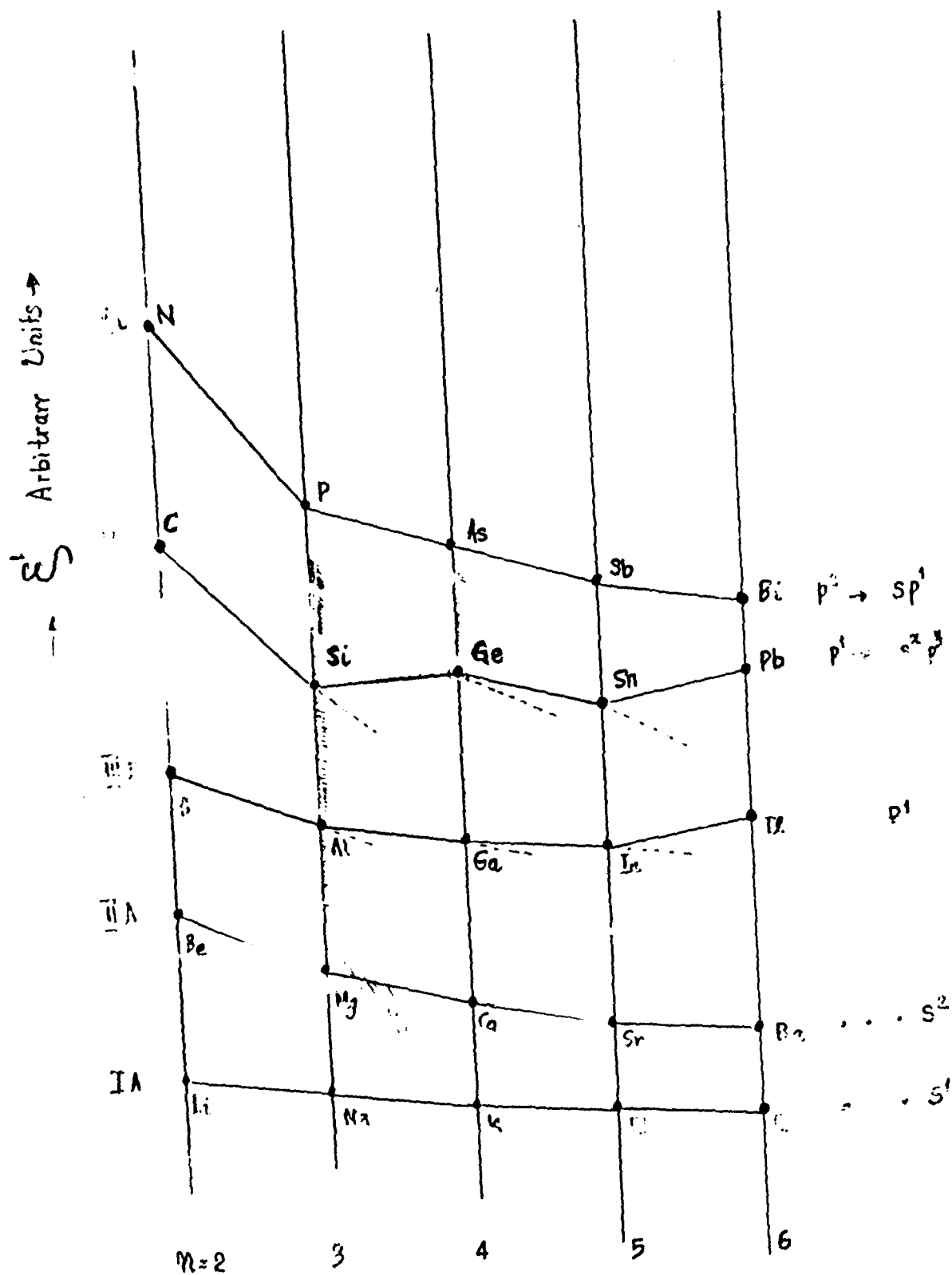
E_d = band theory route

$E_{s.p}$ = Pseudo potential

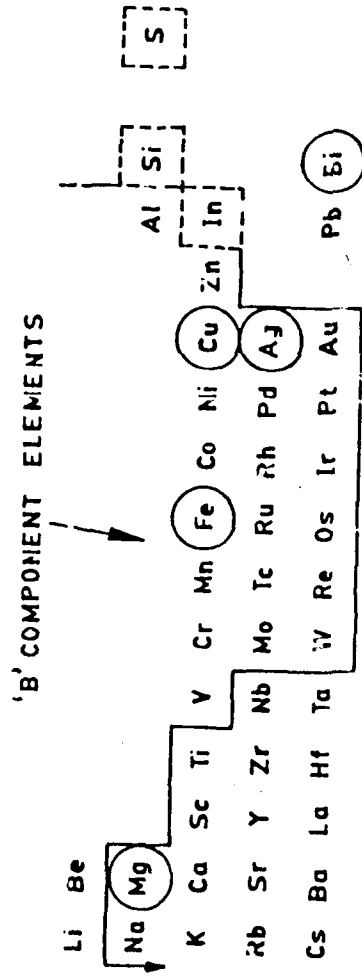
E_{s+d} = Tight binding

E_{others} = Magnetic.





OCCURRENCE OF $MgCu_2$ STRUCTURE



--RAREEARTHS Ce Pr Nd (Pm) Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

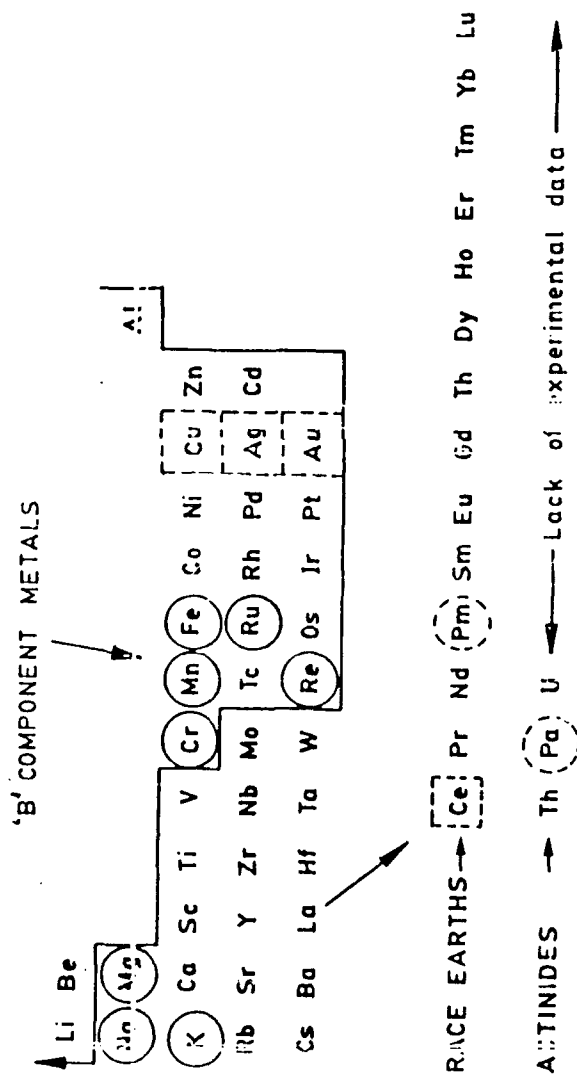
→ACTINIDES Th Pa U Np Pu Am Cm → Lack of data →

(X) BOTH 'A' AND 'B' ELEMENTS

(X) PREDICTED NOT TO FORM $MgCu_2$ STRUCTURE

(X) PREDICTED TO FORM $MgCu_2$ WITH SUITABLE 'B' ELEMENT $ThIn_2$, $ErSi_3$, DrS_7 , $AgBe_2$, $FeBe_2$, $CuBe_2$, $LiPt_2$ ARE SPECIAL CASES.

OCCURRENCE OF $MgZn_2$ STRUCTURE



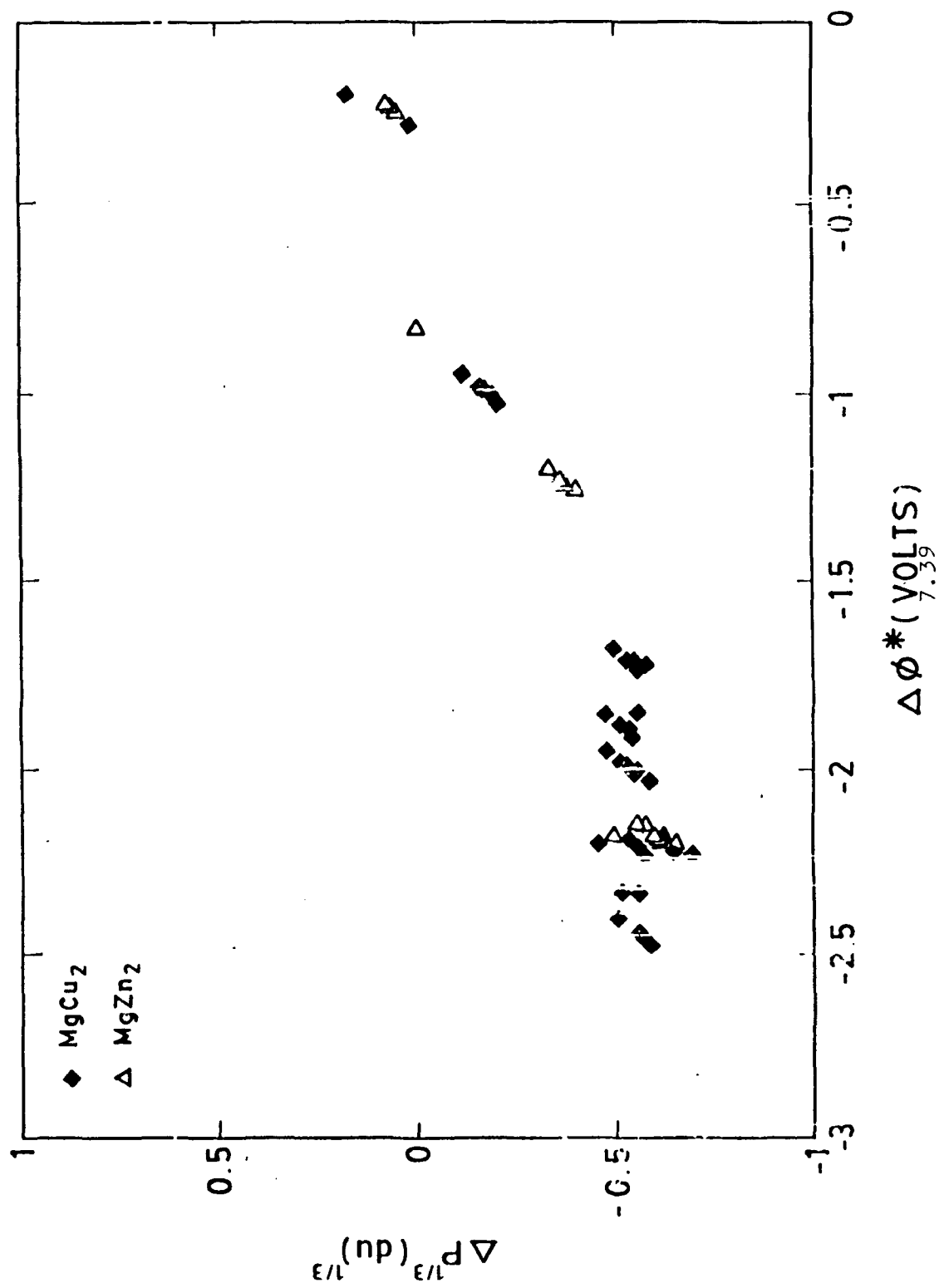
(X) BOTH 'A' AND 'B' ELEMENTS

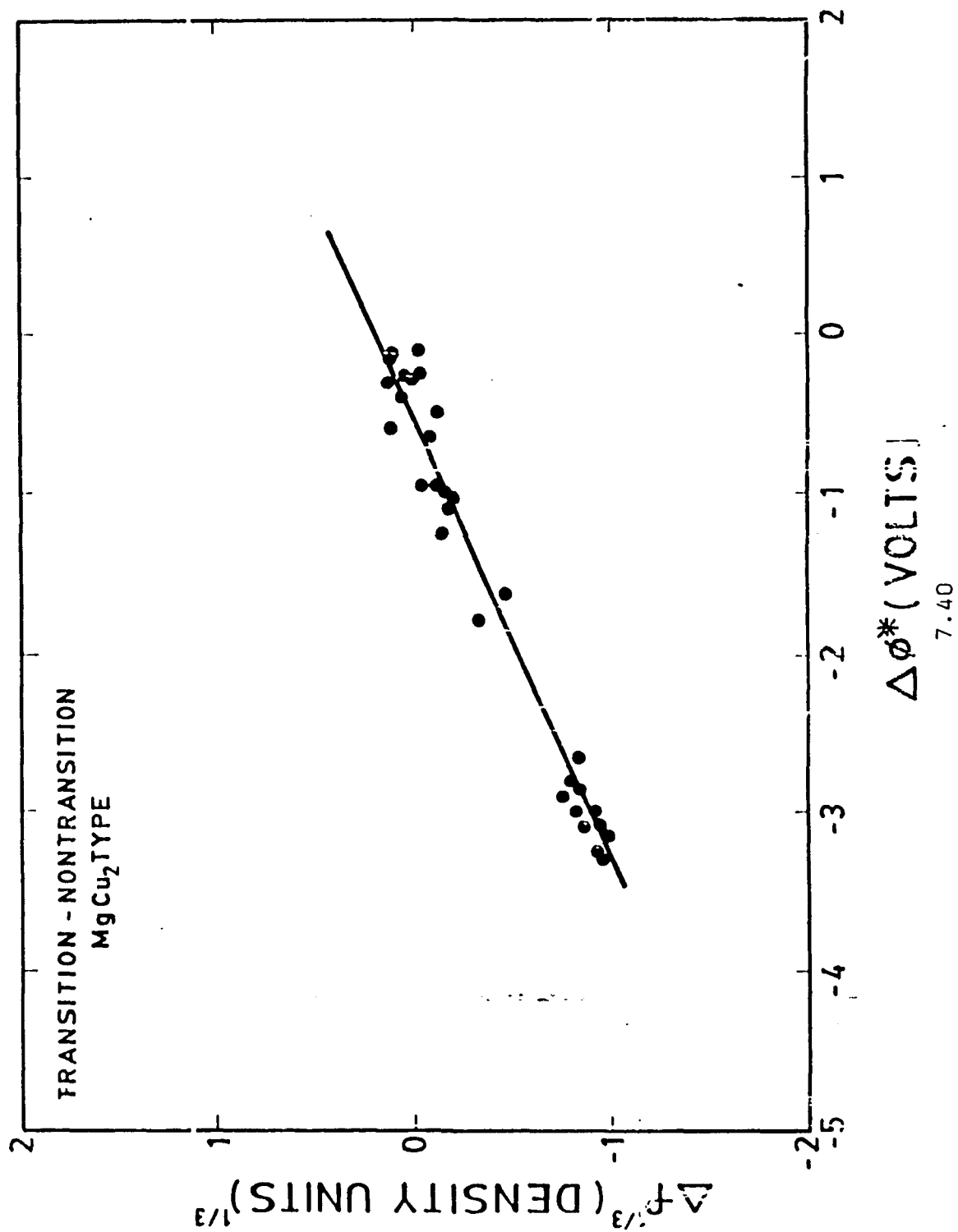
[X] PREDICTED TO FORM $MgCu_2$

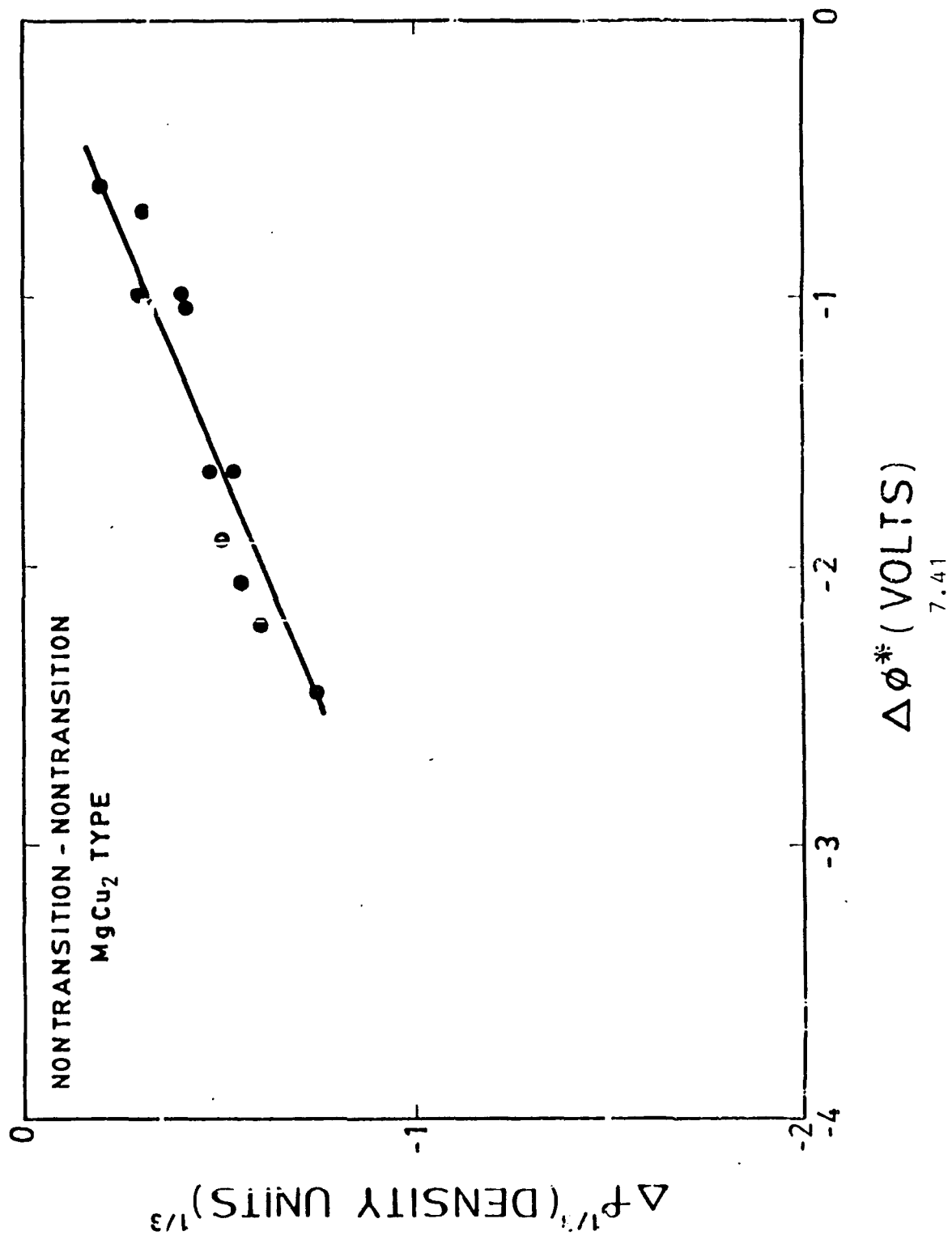
(X) PREDICTED TO FORM $MgZn_2$

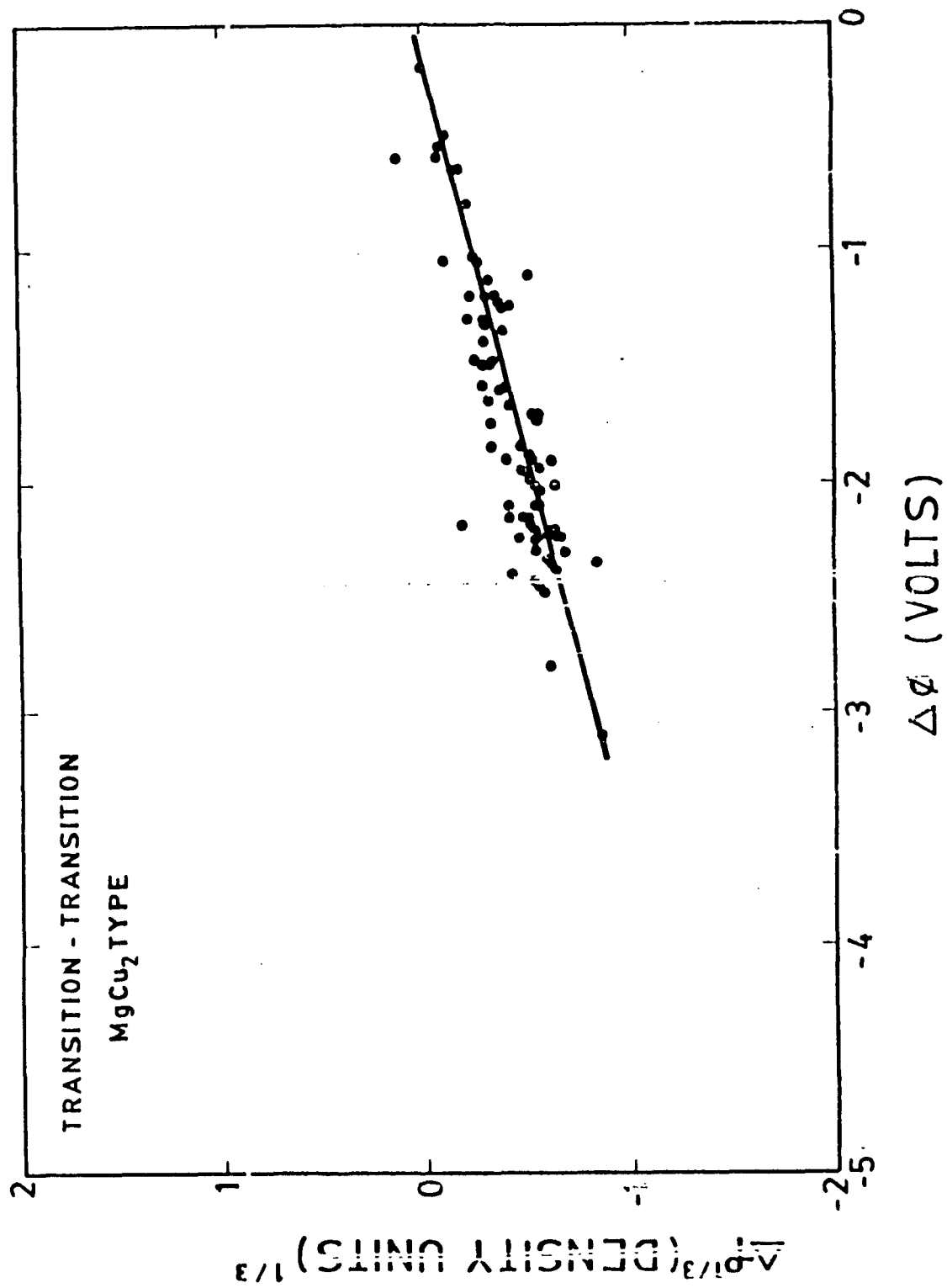
Cr, Mn, Fe, Ru, Re FORM 'A' ELEMENTS ONLY WITH Be as 'B'

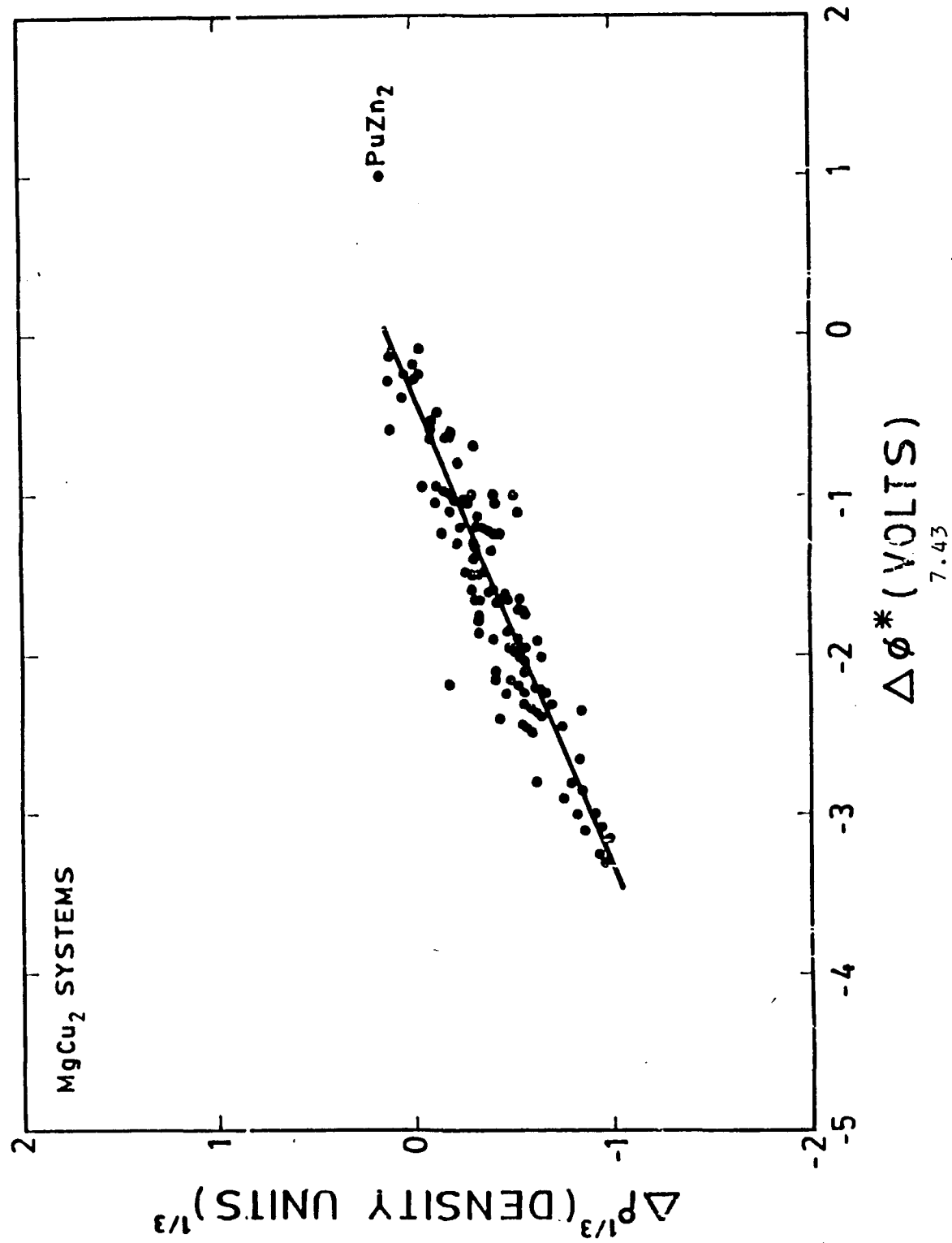
$CaLi_2$ SPECIAL CASE

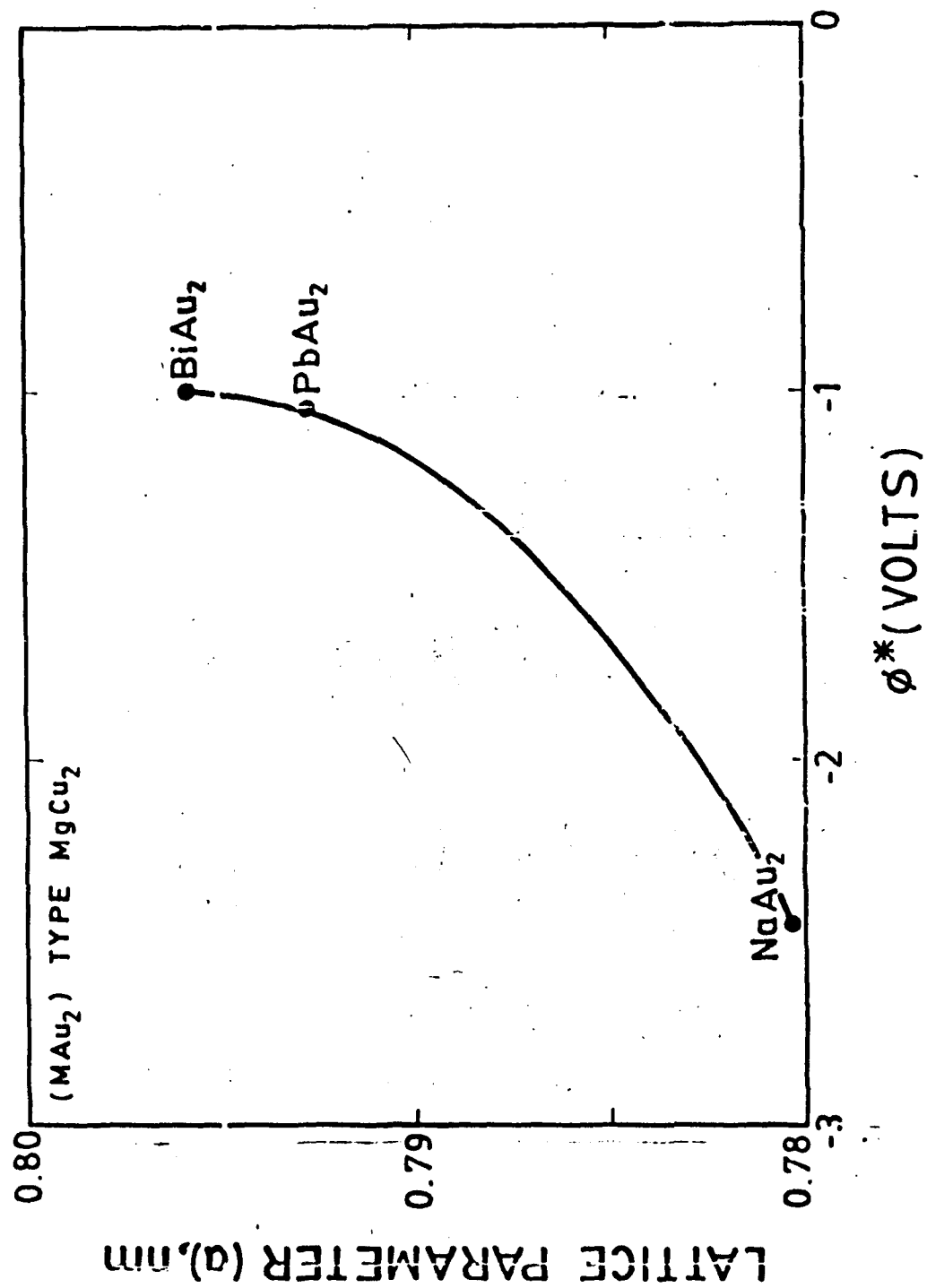


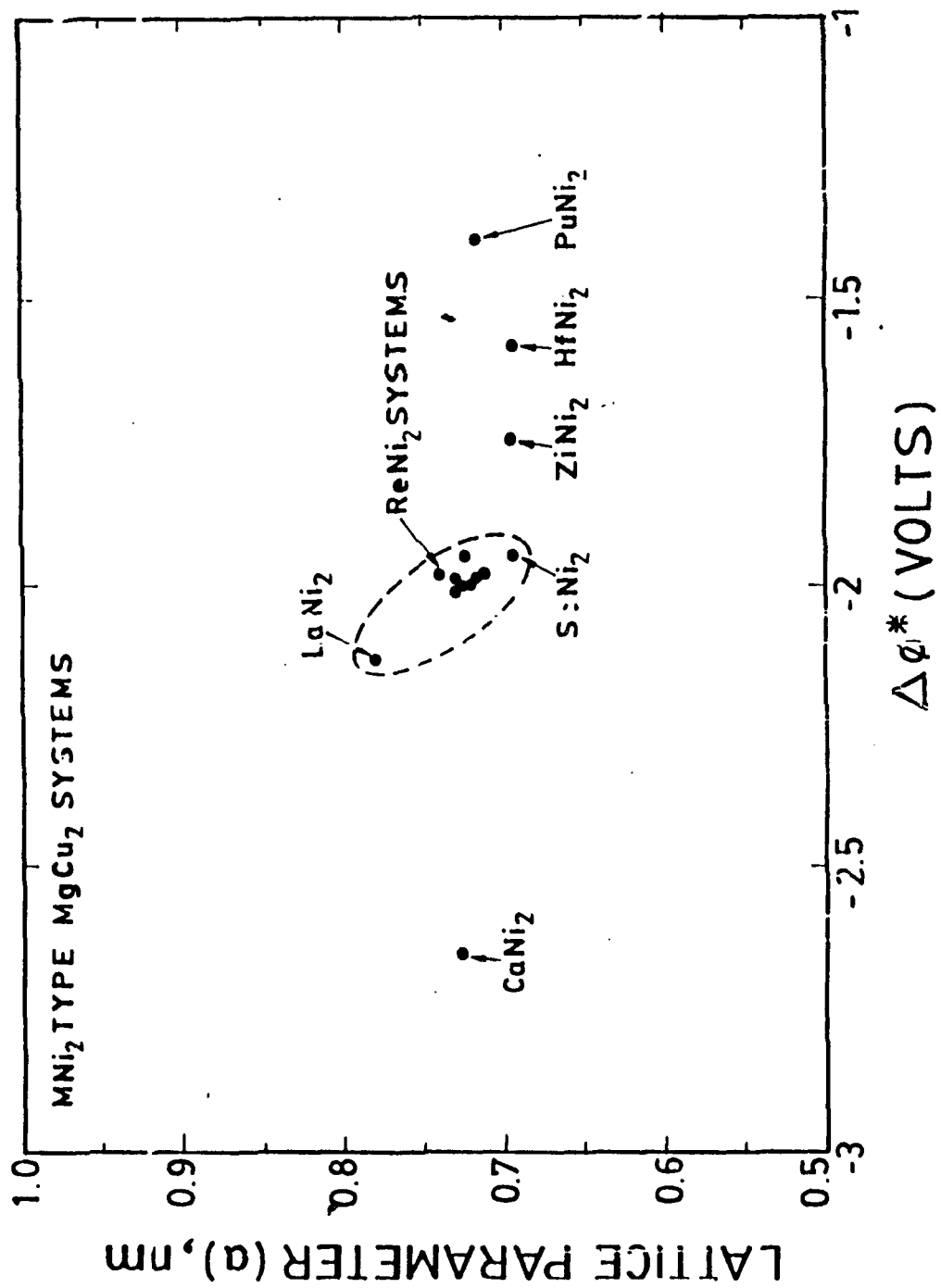


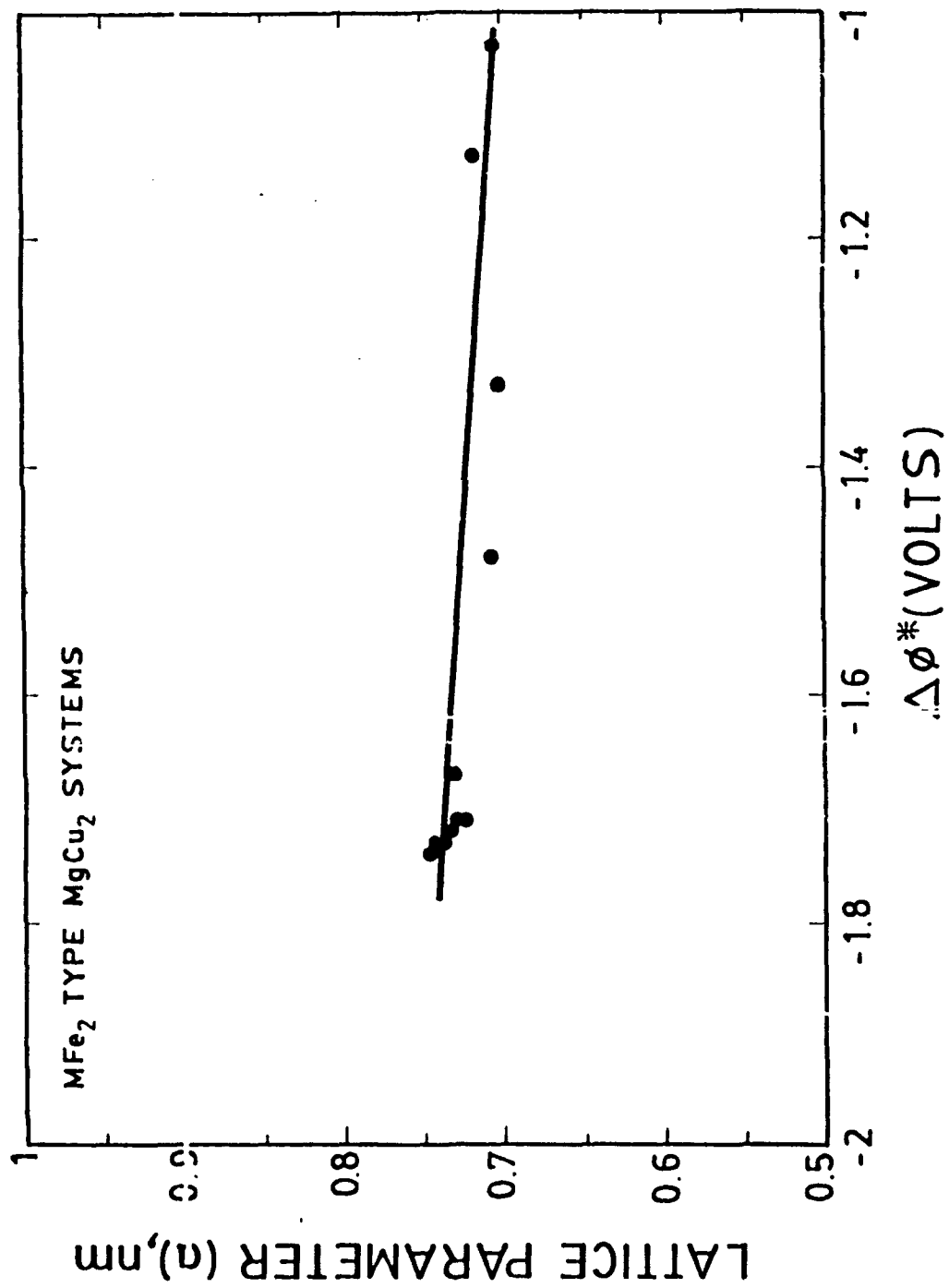


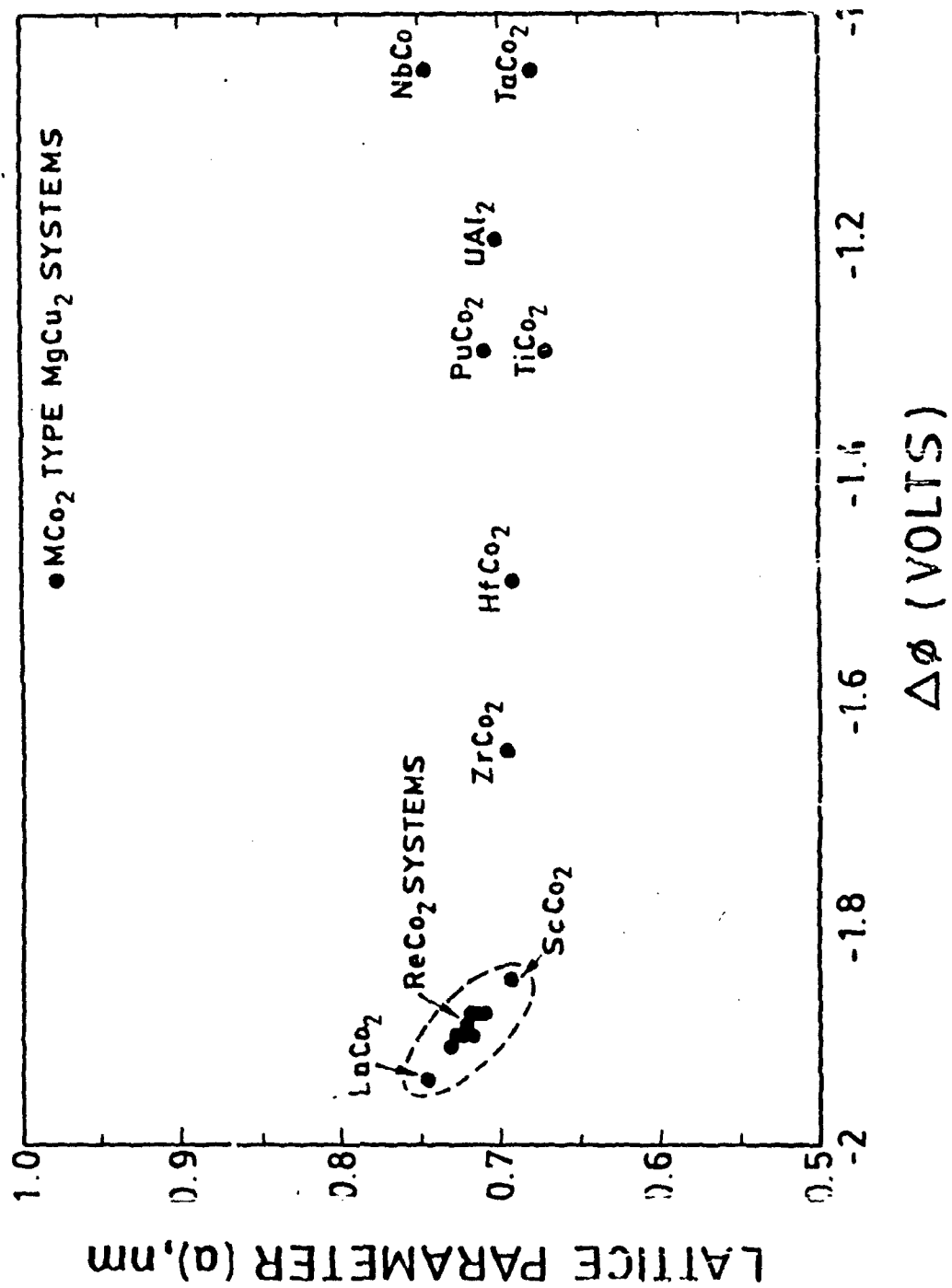


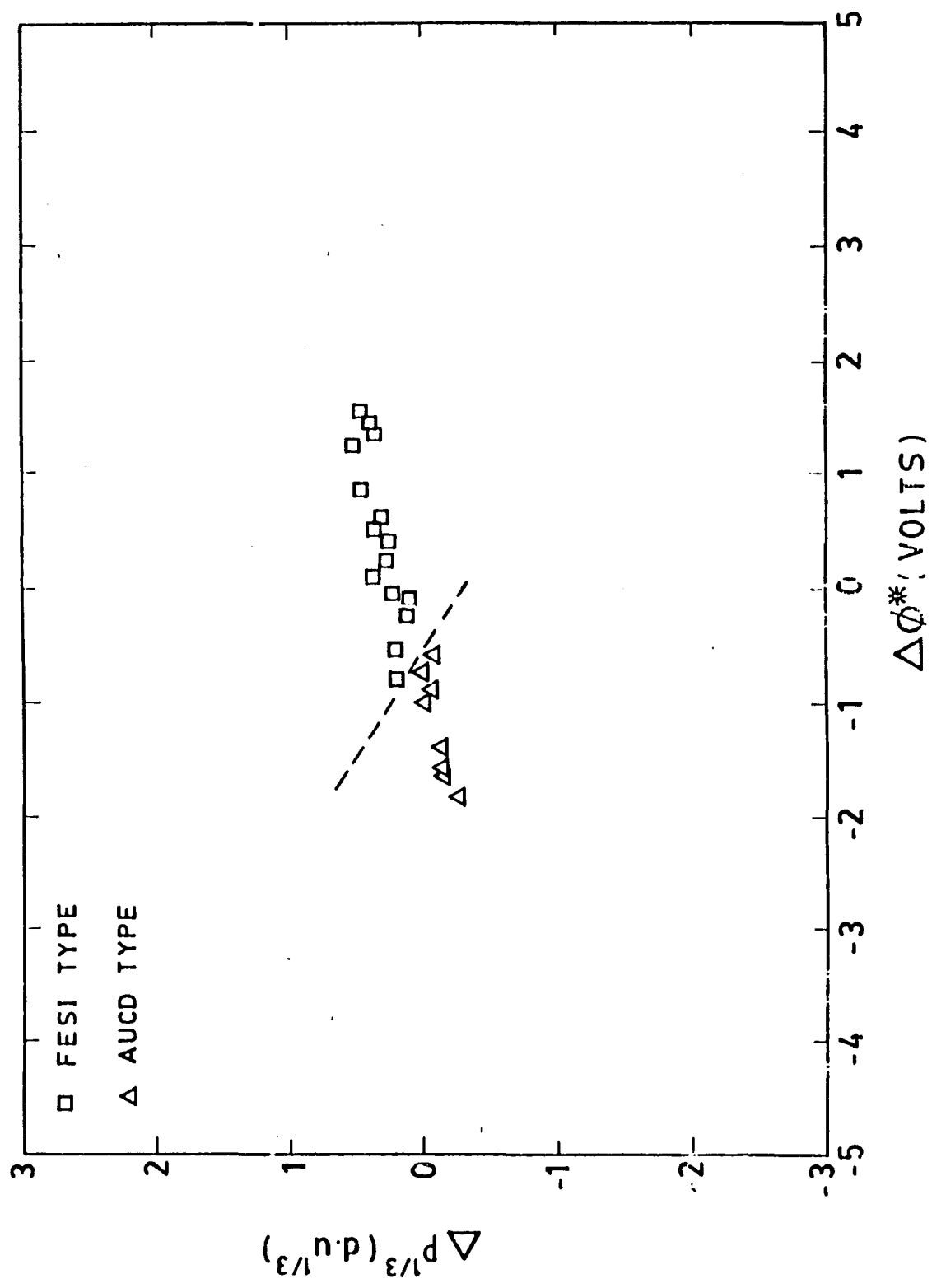




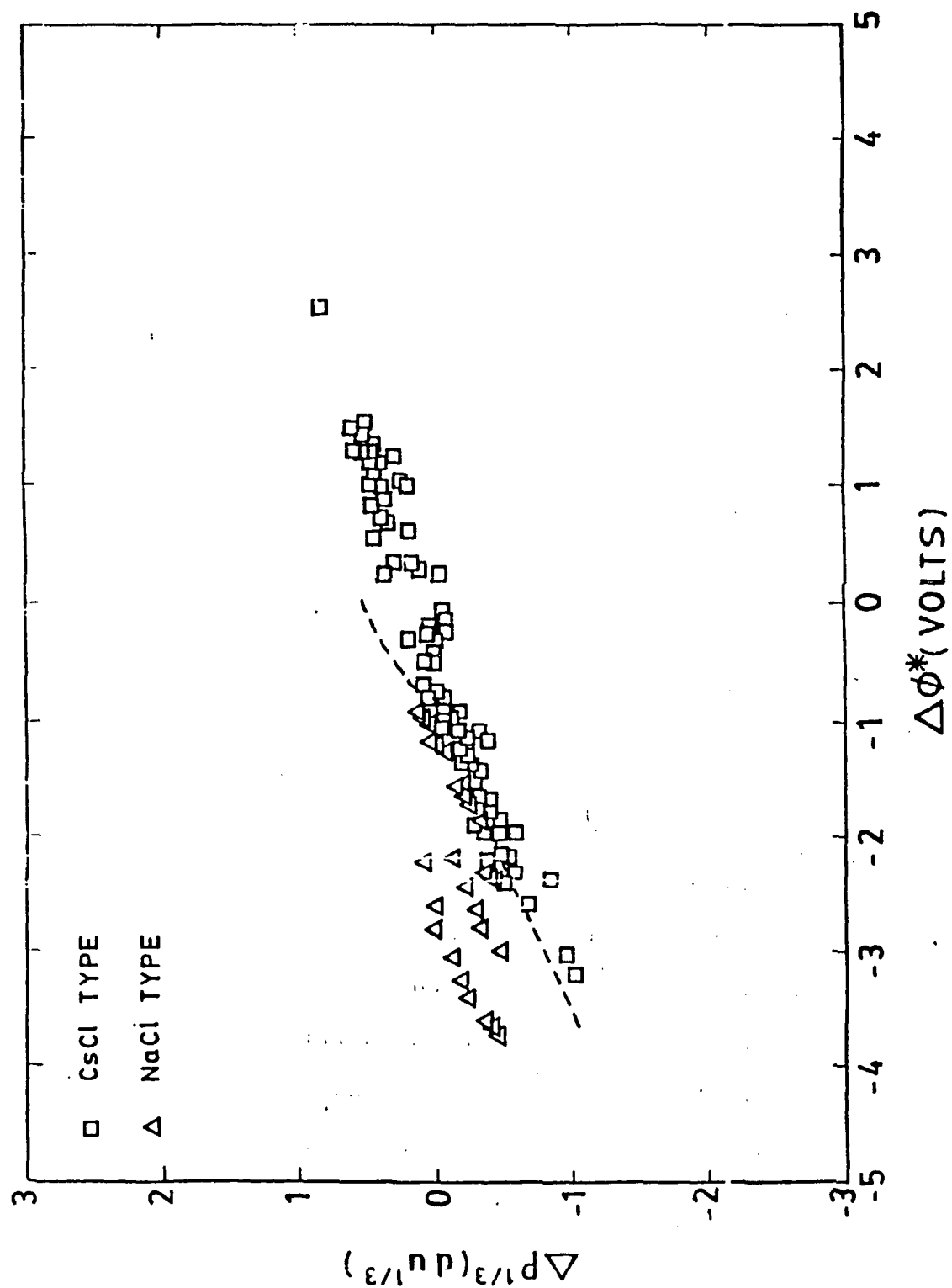








7.48



$\Delta\phi$ (volt)

1.0

0.0

-1.0

-2.0

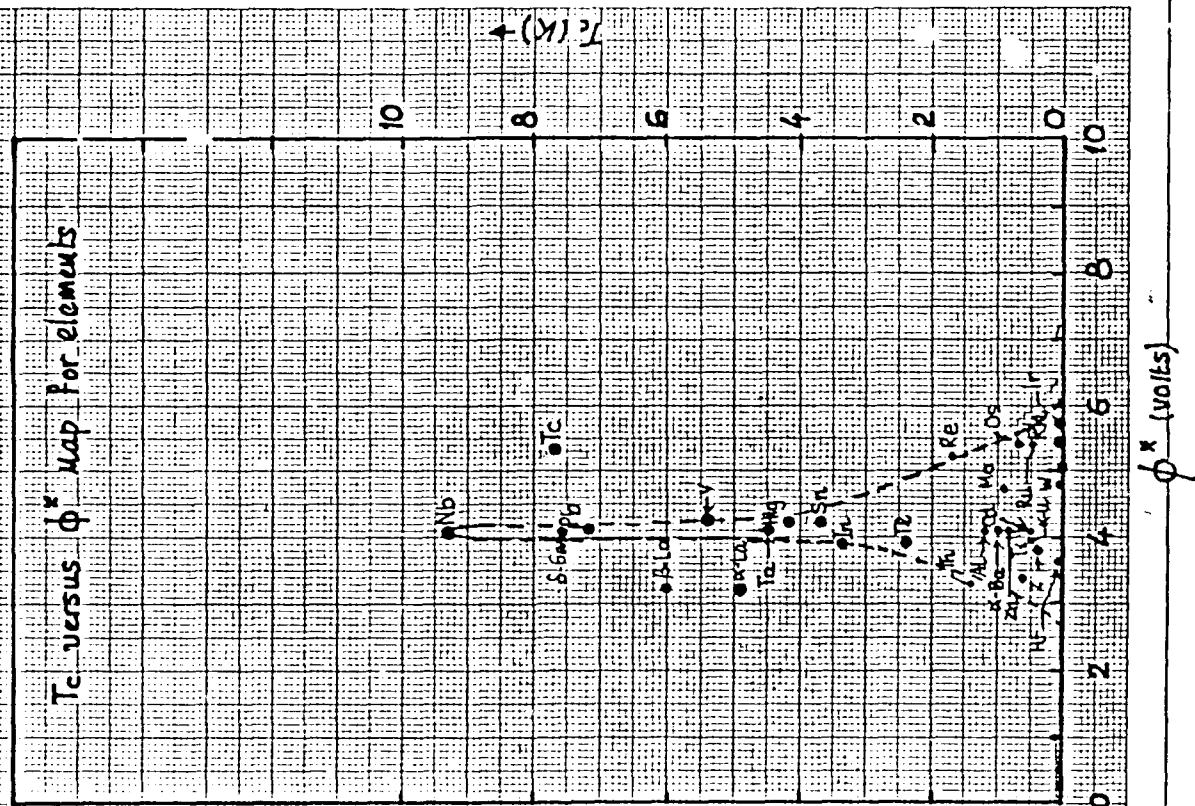
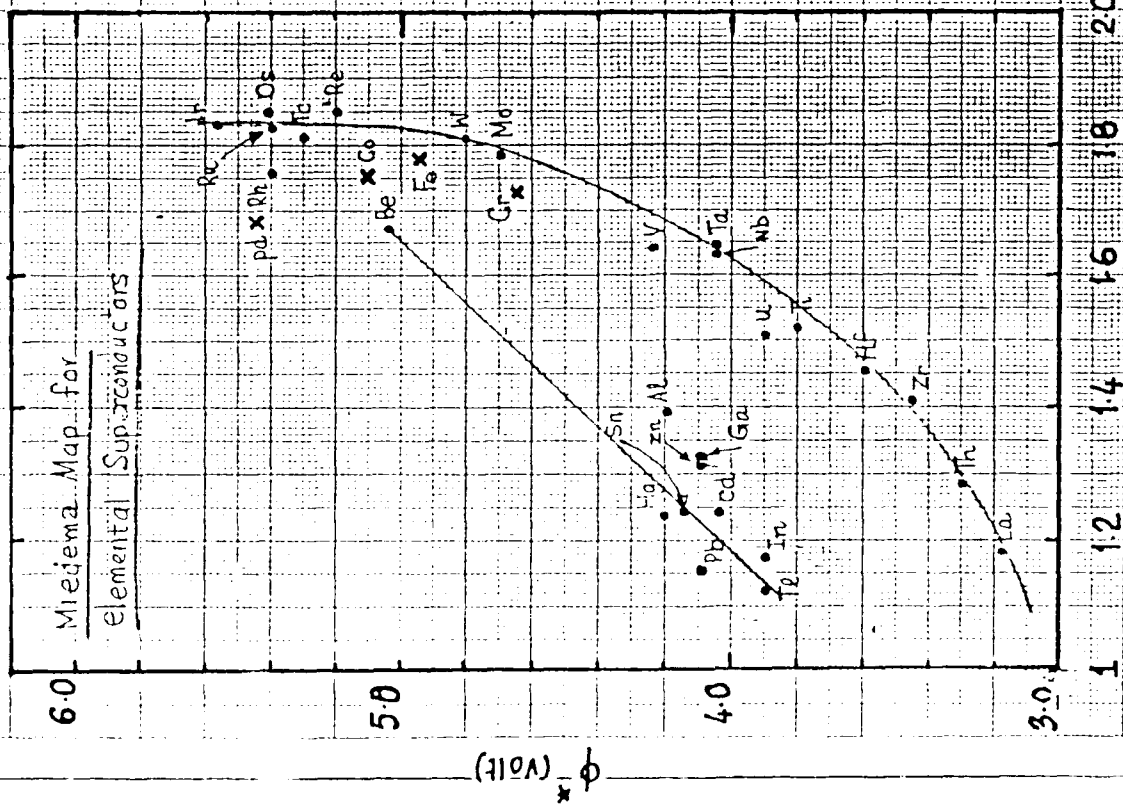
• class II A15
x class I A15

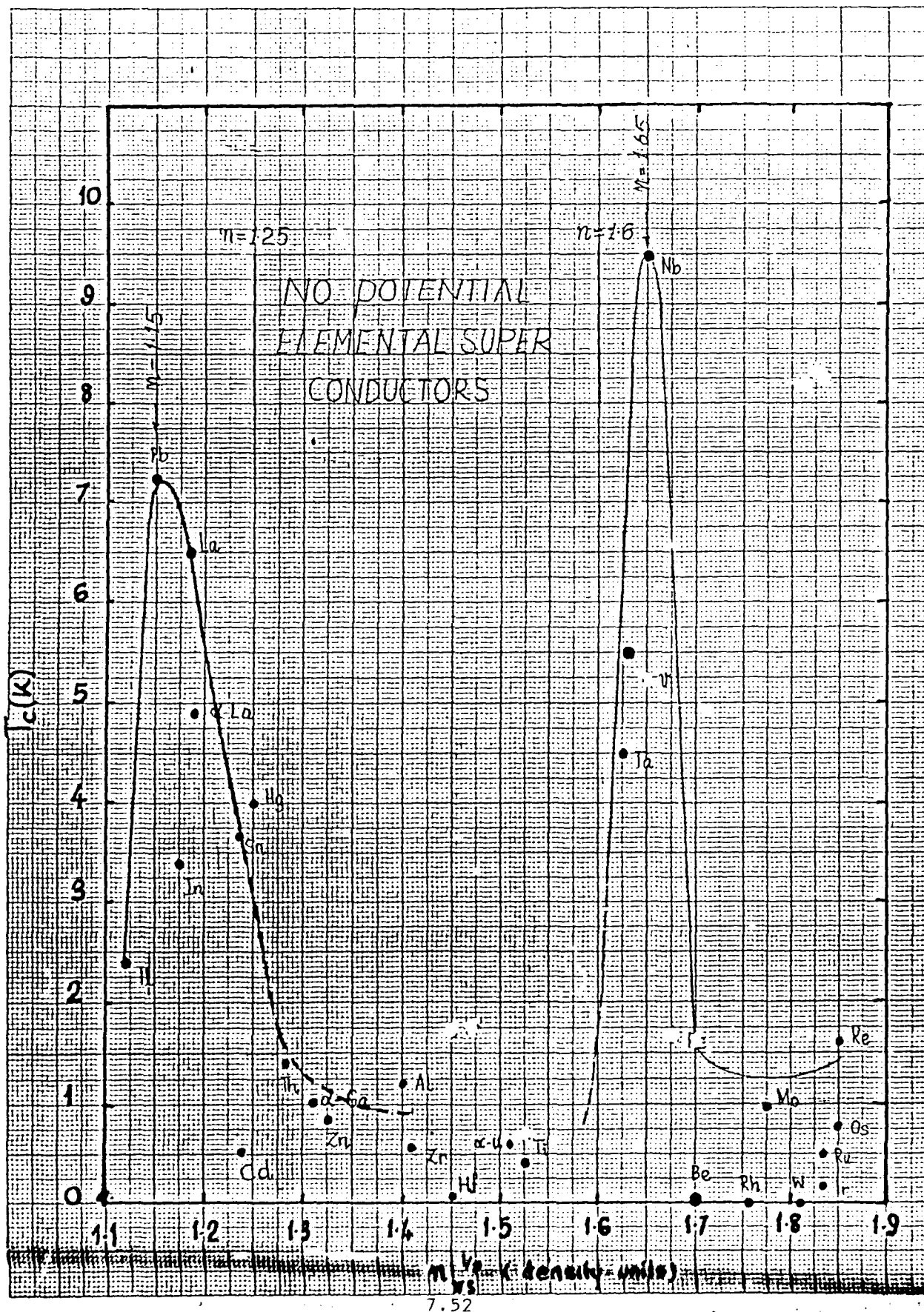
$\Delta n^{1/3}_{WS}$ (density units)

-0.5

0.0

0.5





CONCLUSION # 1

The direct method is seldom
transparent and transferable

but

It offers to validate or otherwise
a successful empirical correlation

CONCLUSION # 2

Miedema coordinates : Bond Indicators?
STRUCTURE SORTING
PARAMETERS

Pettifor's vs Miedemas