JPL

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SUTTERUDITES FOR THERMOELECTRIC APPLICATIONS

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by

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State-of-the-art thermoelectric materials

ZT =1 limit but much larger ZT values are theoretically possible

Applications of Improved Thermoelectric Materials

- Improved performance could open up wide market for thermoelectric devices
  - Power Generation
    - Waste heat recovery (automobile, industrial processes..)
    - Space Power (RTGs, microRTGs)
  - Cooling
    - Thermal management (high power electronic devices)
    - Air conditioning (ship, automobile..)
    - Refrigeration (consumer appliances..)
  - Sensors

Approaches to Find More Efficient New Thermoelectric Materials

Conventional semiconductors

- Binary compounds
- Ternary and more complex compounds

Unconventional semiconductors

- Non conventional transport properties

Heterostructures

- Superlattices
- Quantum wells

Current JPL activities in Thermoelectrics

Materials

- Preparation, characterization, analysis and modeling of new thermoelectric materials
  - Skutterudites, other compounds and alloys
- Measurement of transport properties of semiconductors
  - 4K-1300K temperature range

Devices

- Testing of thermoelectric power generating devices
  - SP-100 multicouple cells

Modeling

- Modeling of transport properties
  - Computer models to predict ZT

New Materials: Exploratory Search

- The search for thermoelectric materials with high ZT values is guided by a certain number of criteria, including:
  - Semiconducting properties
  - Large Seebeck coefficient
  - High carrier mobility, high electrical conductivity
  - Low lattice thermal conductivity
  - Chemical stability and low vapor pressure
  - Band gap > $4k_BT$ at operating temperature

Selection of high performance thermoelectric materials necessitates striking a balance between conflicting requirements for the optimization of the various transport properties.

Existence of Skutterudites

- JPL Exploratory search identified skutterudite family

  Binary Compounds
  - Nine semiconducting and two metallic compounds

  Solid solutions
  - Found solid solutions exist between most binary skutterudites as well as in many other systems

  New phases are derived from binary compounds
  - By replacing the transition metal or the pnicogen or both elements
  - By conserving the number of valence electrons
  - Numerous related skutterudite phases exist

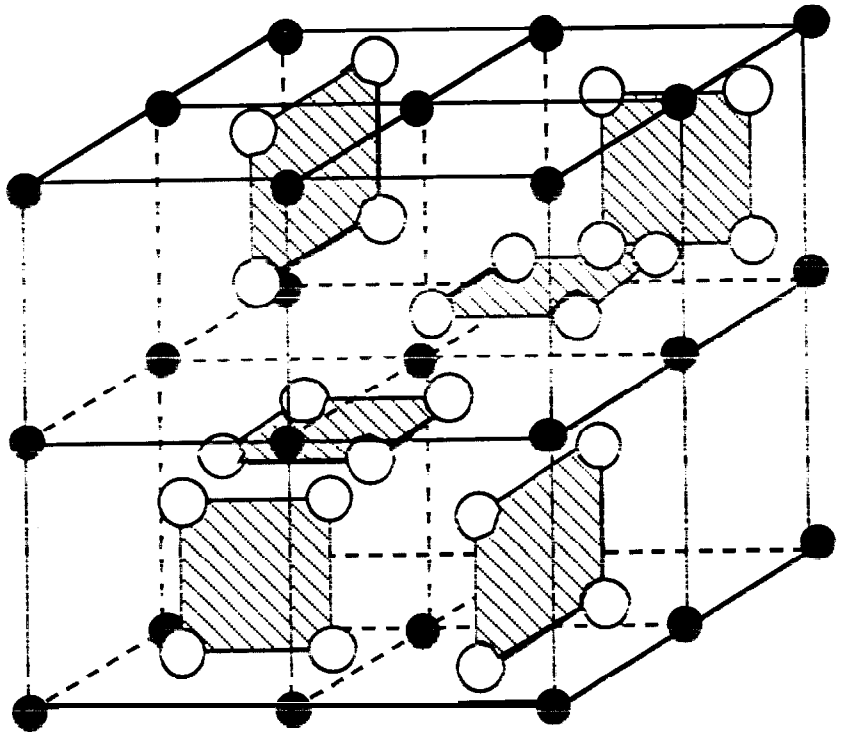
  Filled skutterudites
  - Literature data show that filled skutterudites can be formed
  - By filling the two empty octants present in the 32 atoms unit cell
  - The number of valence electrons needs to remain constant to conserve a semiconducting behavior

JPL Programs on Skutterudites A Systematic Study in Progress

- Investigating basic properties of skutterudites materials
  - First study binary compounds
  - Then ternary/quaternary isostructural phases
- Conducting experimental and theoretical studies
  - Decomposition temperature, atomic composition
  - Band gap, Debye temperature, thermal expansion, Grüneisen constant
  - Thermoelectric properties
    - Seebeck coefficient
    - Carrier mobility
    - Lattice thermal conductivity
    - Doping level

To obtain best compositions for maximum ZT

Skutterudite Crystal Structure



. T: transition metal

O P.: pnicogen

Tools to Study Skutterudite Compositions

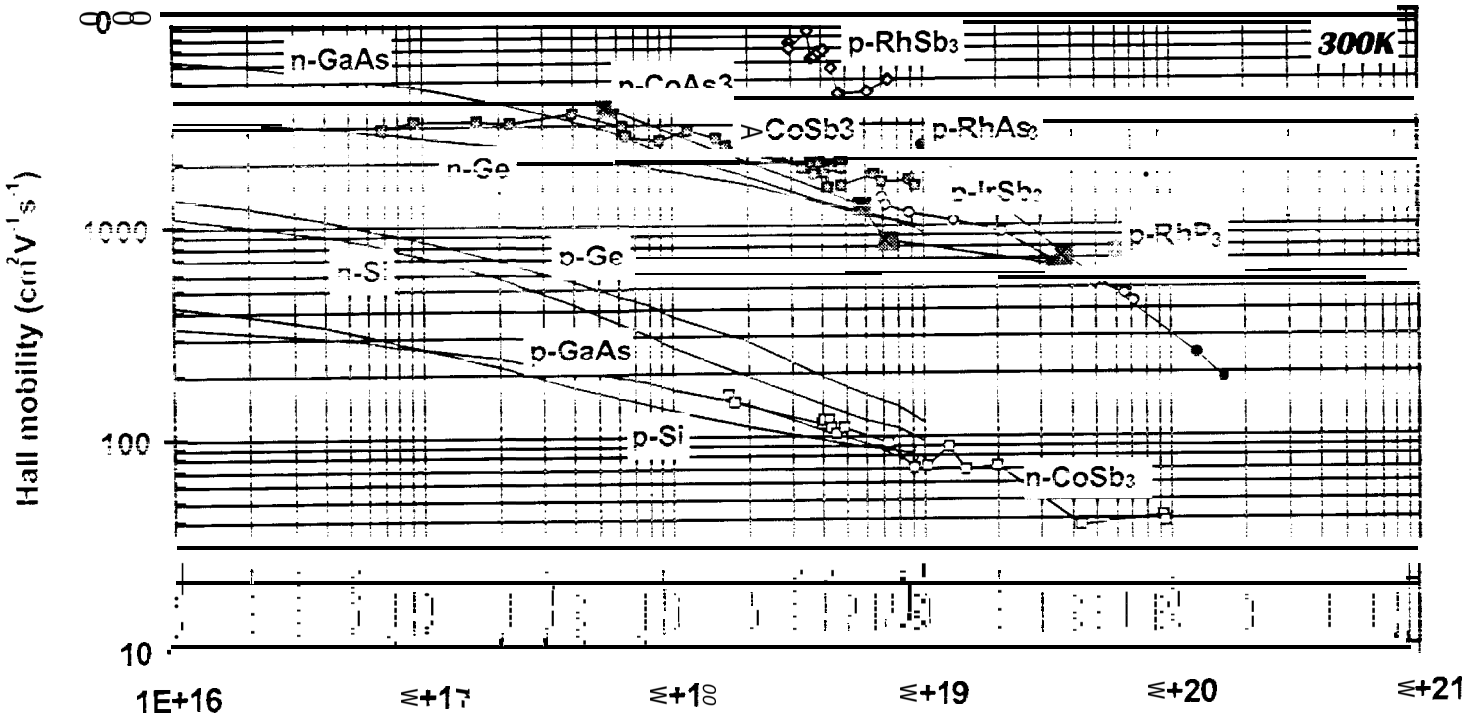
- Materials preparation
  - Single and poly- crystalline samples
  - From the melt (some binary compounds)
  - Using powder metallurgy techniques (all other compounds)
- Measurements: electrical and thermal transport properties
  - Hall effect, electrical and thermal conductivities, Seebeck coefficient
  - From 4K to 1200K
- Analysis and modeling of variations in transport properties
  - As a function of carrier concentration, temperature and composition
  - Also using JPL model developed for several thermoelectric materials
- Calculation of the electronic structure of skutterudites
  - From first principles, using the tight-binding method
  - Electronic structure of dopants, substituting atoms in skutterudites

Binary Skutterudite Compounds

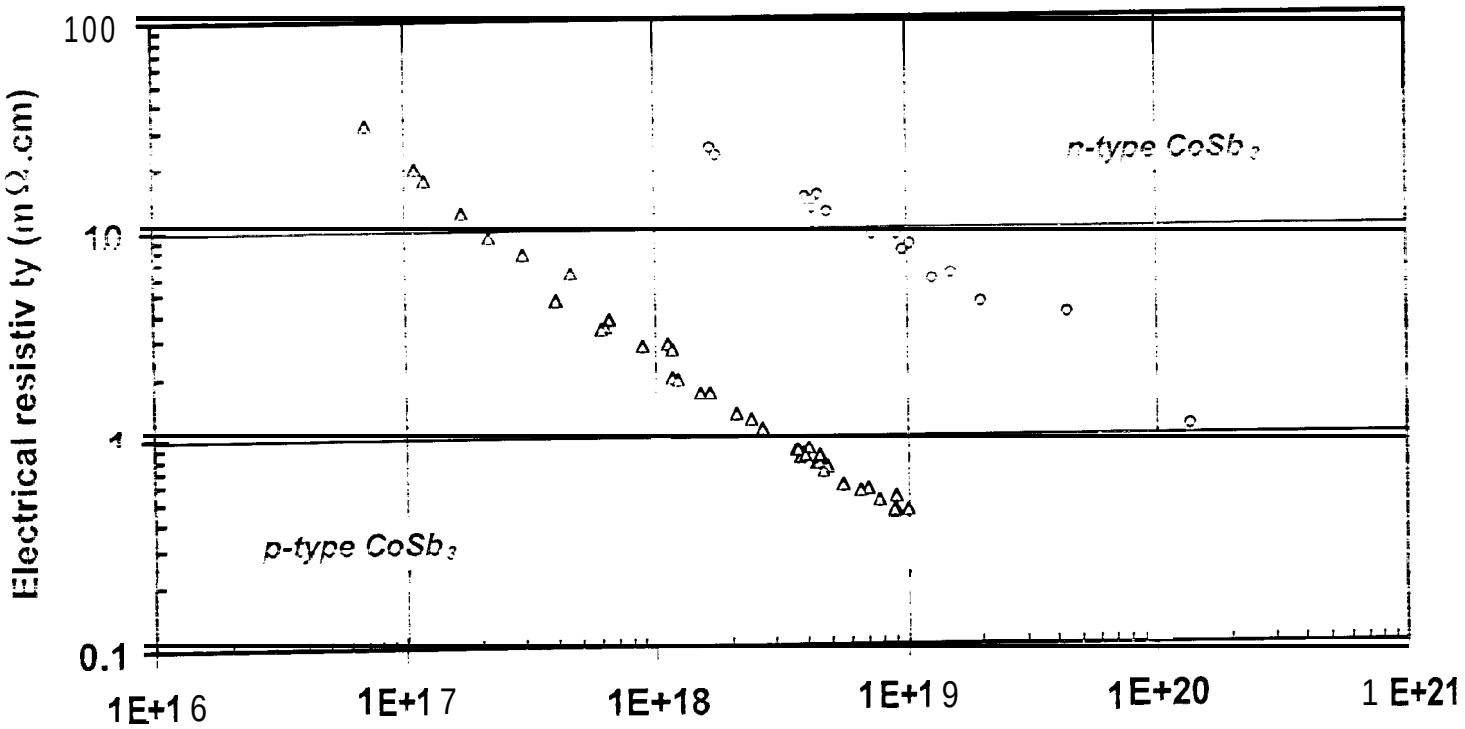
Compound	a (Å)	T_m (°C)	E_g (eV)
CoP_3	7.7073	>1000	0.43*
$CoAs_3$	8.2043	960	0.69*
$CoSb_3$	9.0385	850	0.63*
RhP_3	7.9951	>1200	-
$RhAs_3$	8.4427	>1000	>0.85*
$RhSb_3$	9.2322	900	0.80*
IrP_3	8.0151	>1200	-
$IrAs_3$	8.4673	>1200	-
$IrSb_3$	9.2533	1141*	1.18*
NiP_3	7.819	>850	metallic
PdP_3	7.705	>650	metallic

* JPL findings

Binary Skutterudites 300K Hall Mobility



Binary Skutterudites: $CoSb_3$ 300K Electrical Resistivity



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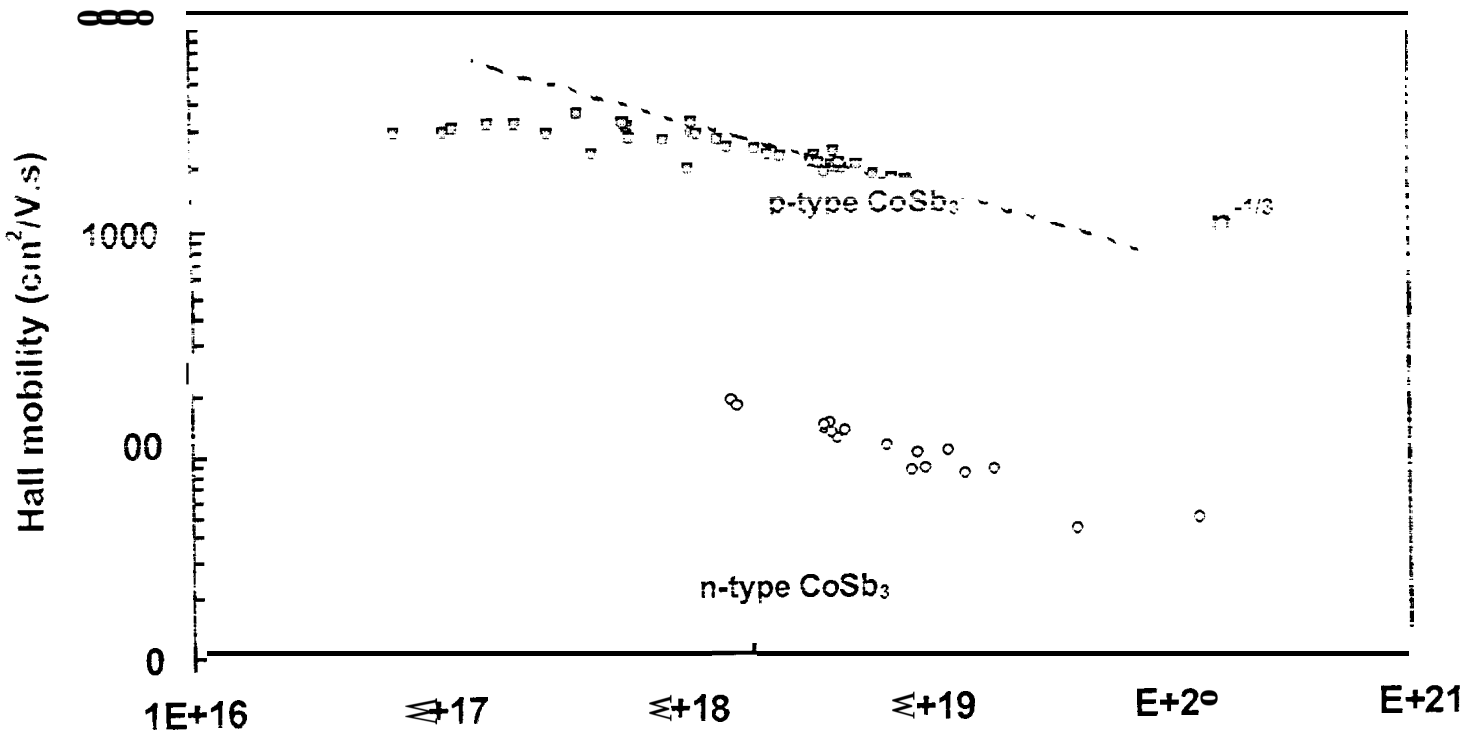
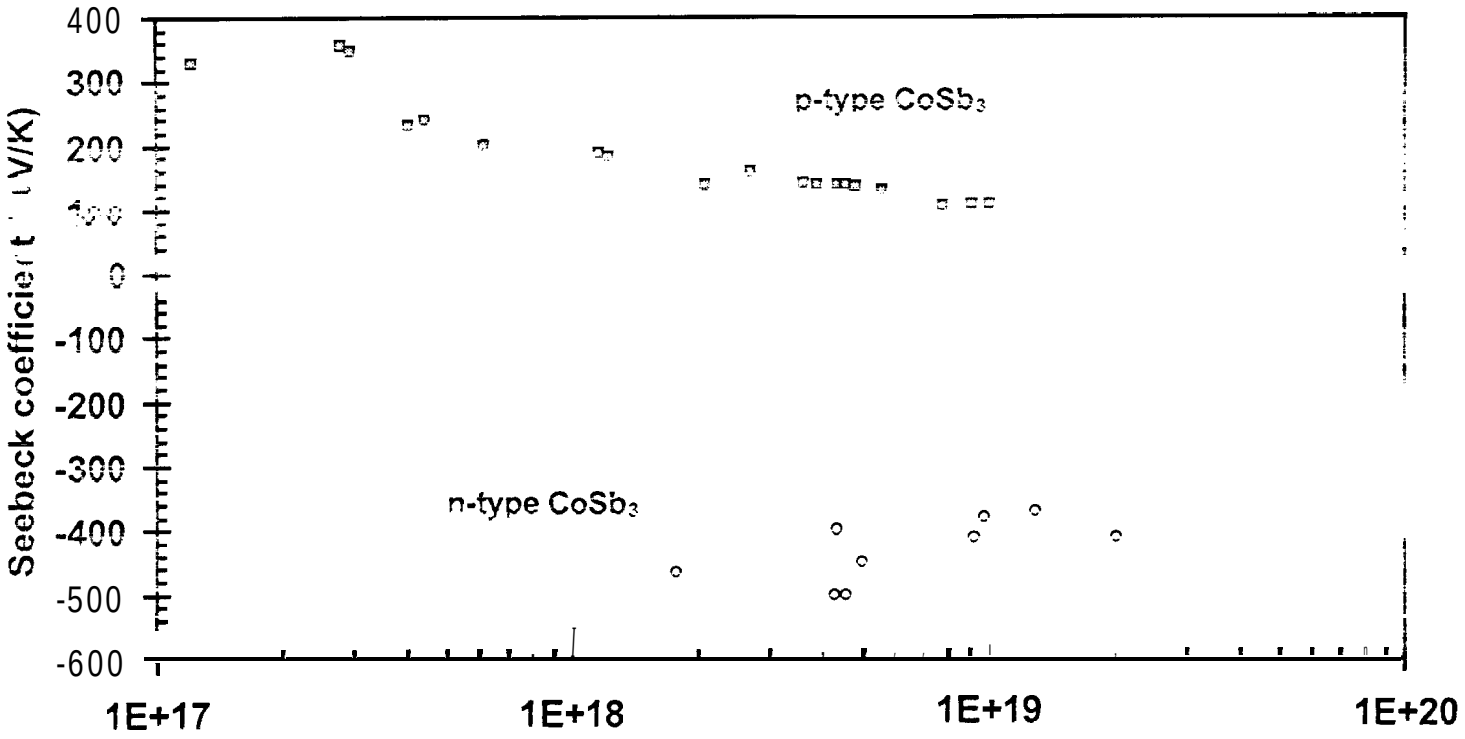
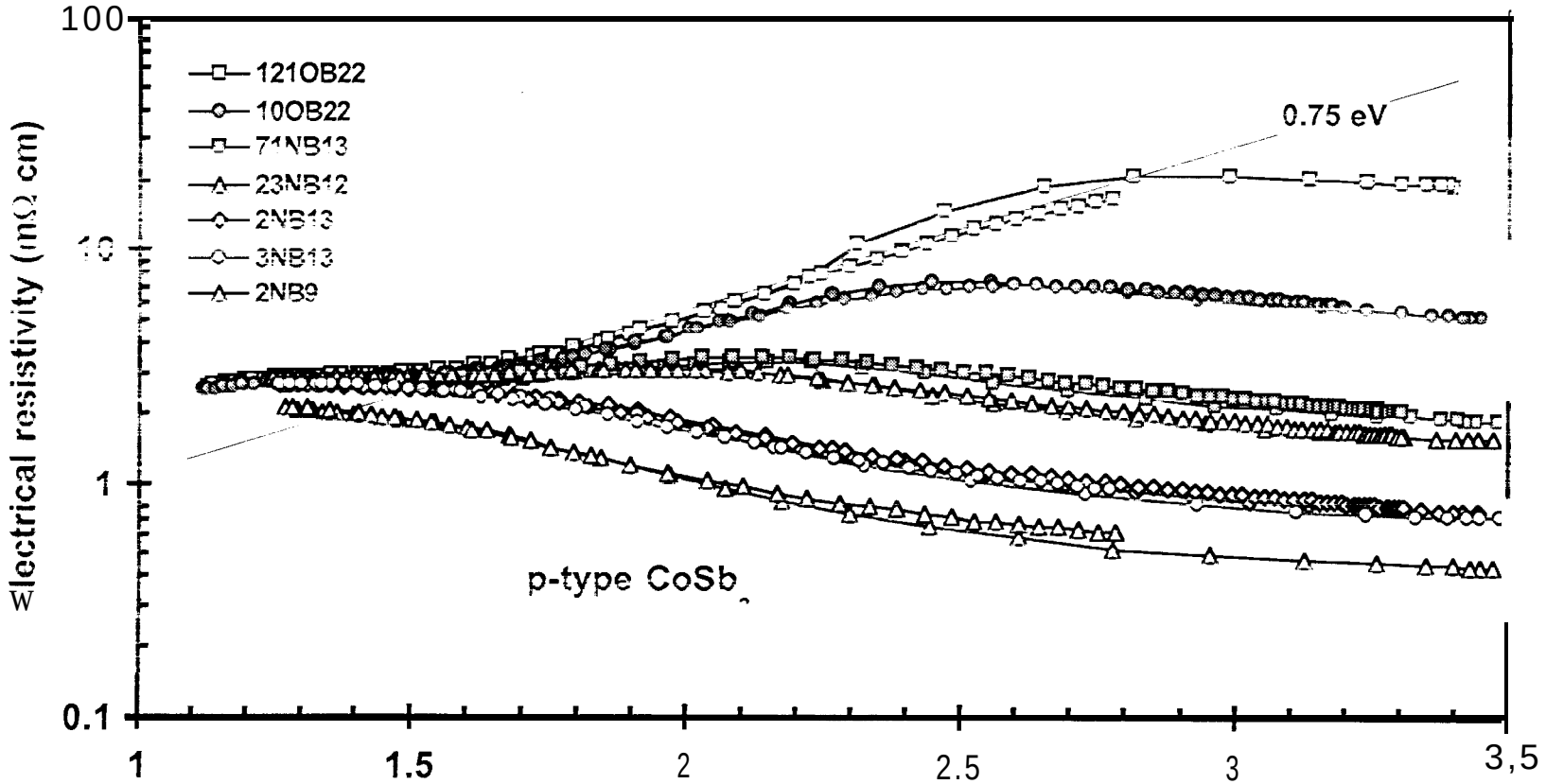


Binary Skutterudites: $CoSb_3$ 300K Seebeck Coefficient



Binary Skutterudites: P-Type $CoSb_3$ Electrical Resistivity vs. T



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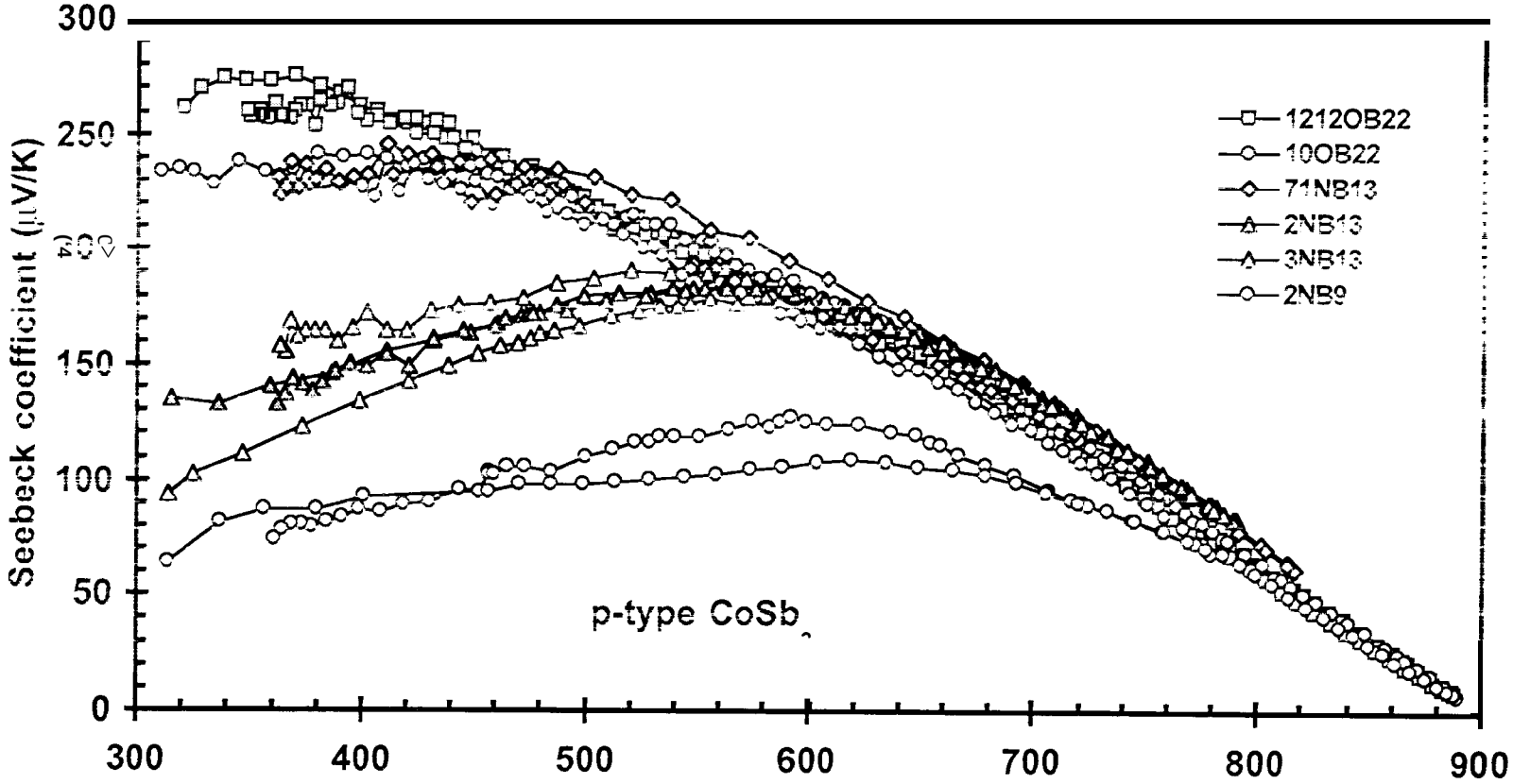
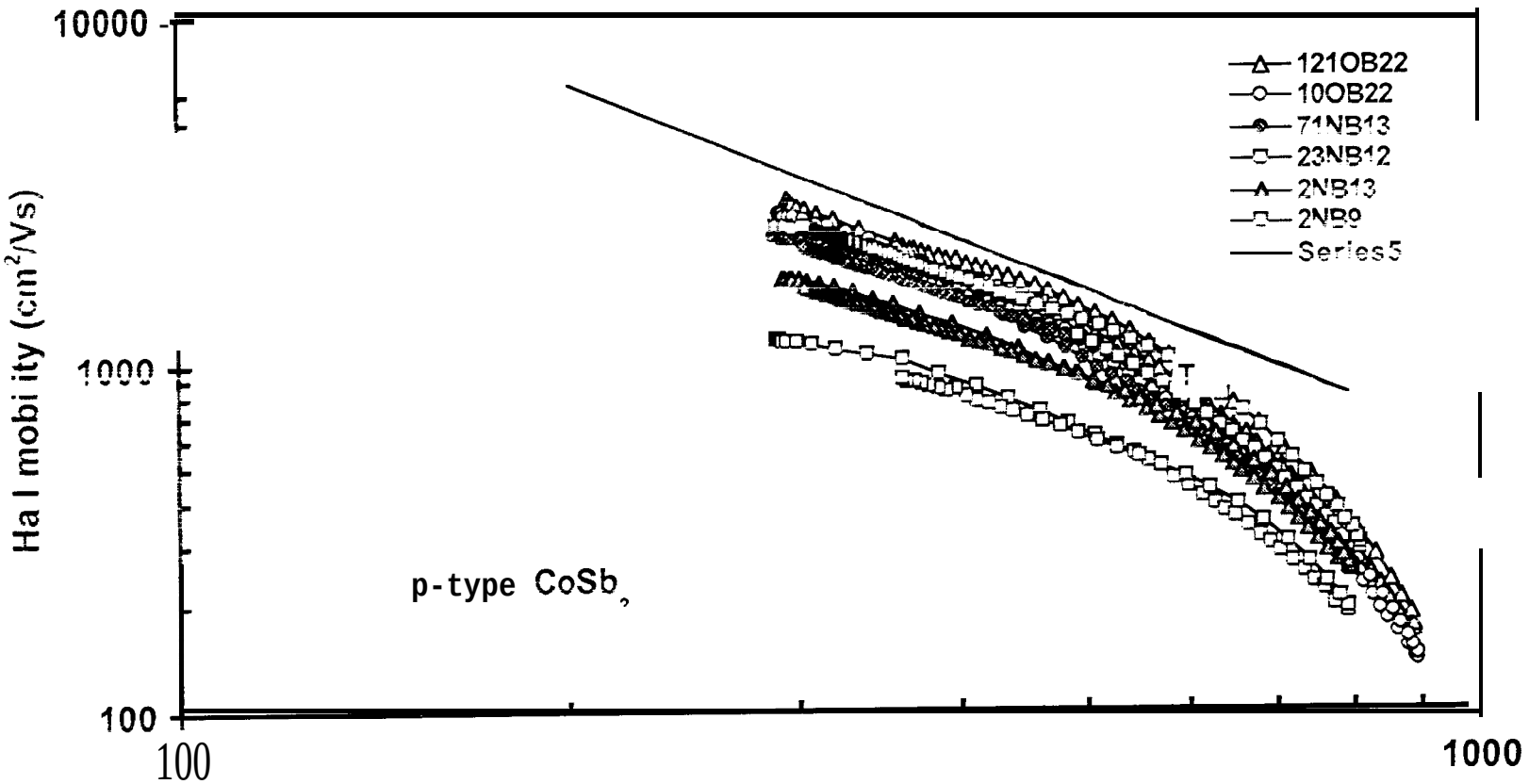
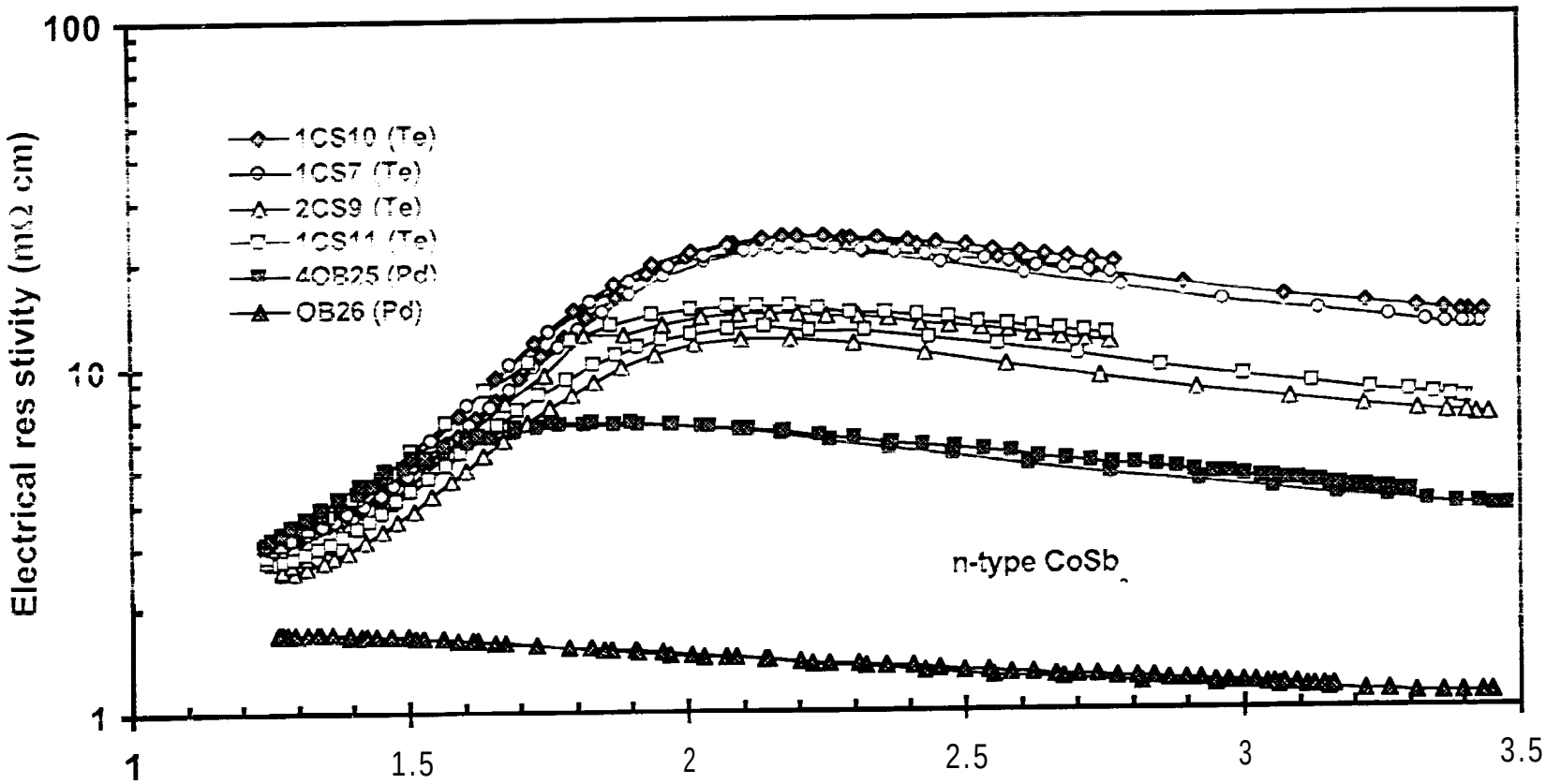


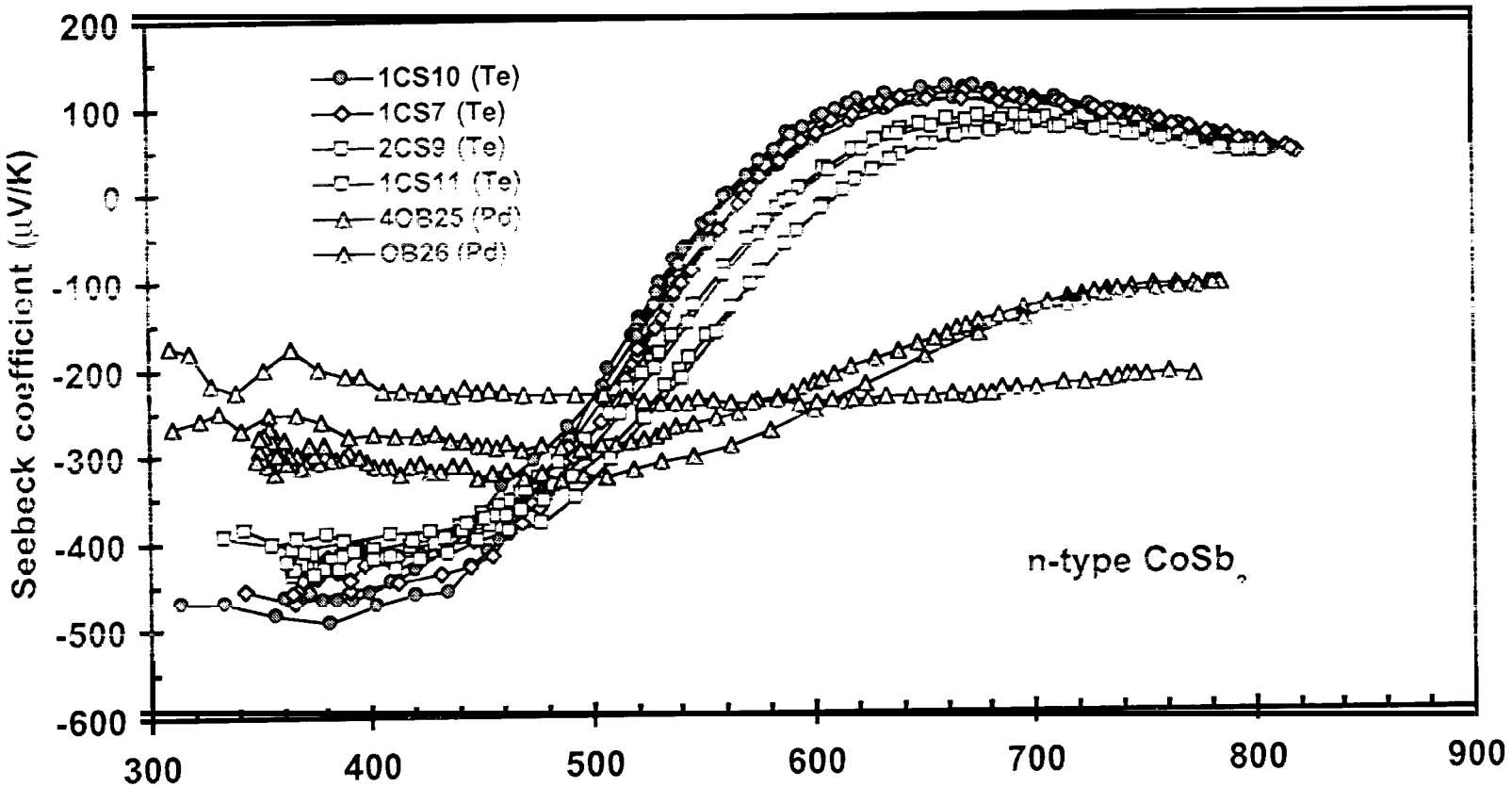
Binary Skutterudites: P-Type $CoSb_3$ Hall Mobility vs. T



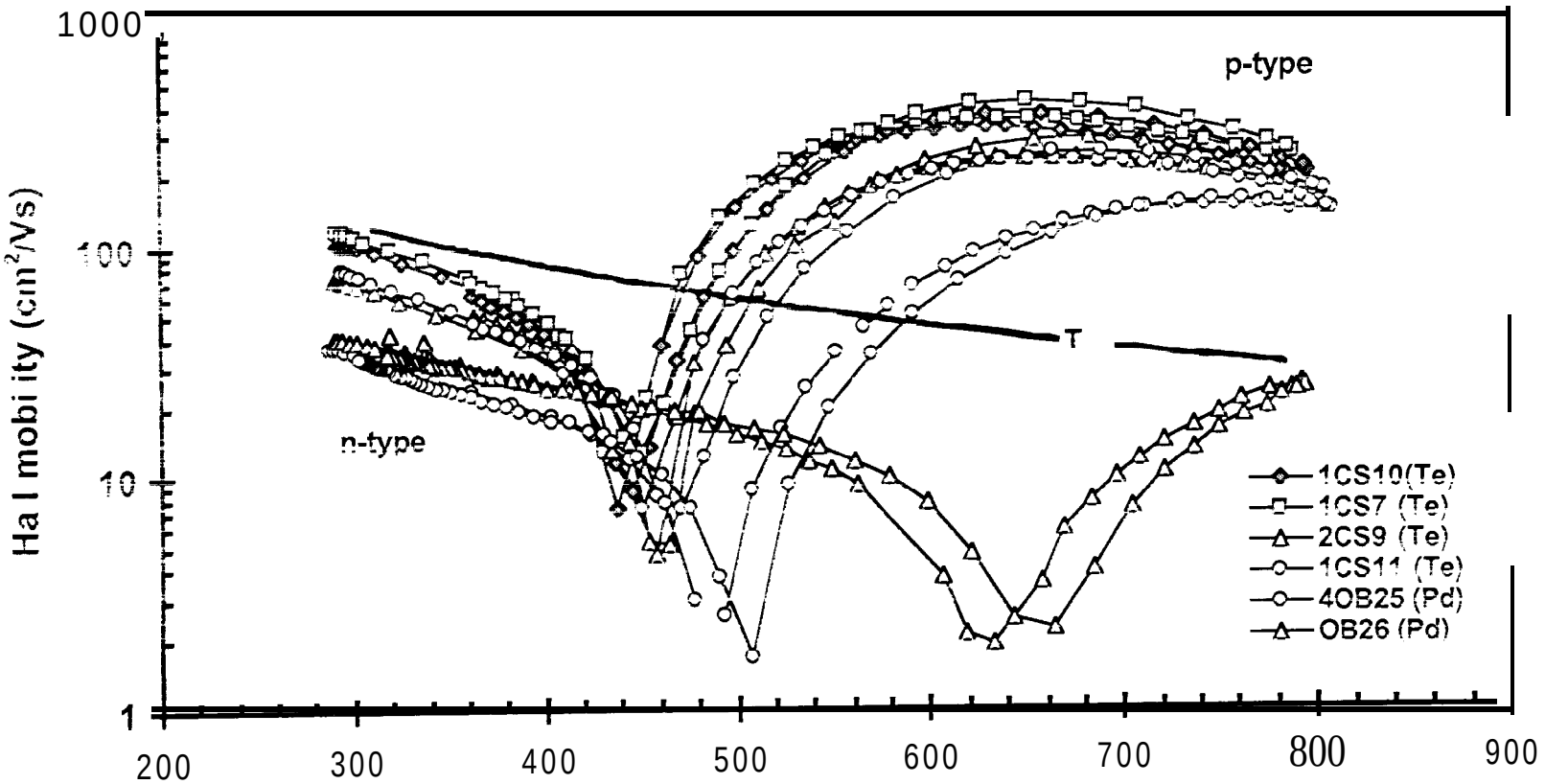
Binary Skutterudites: N-Type $CoSb_3$ Electrical Resistivity vs. T



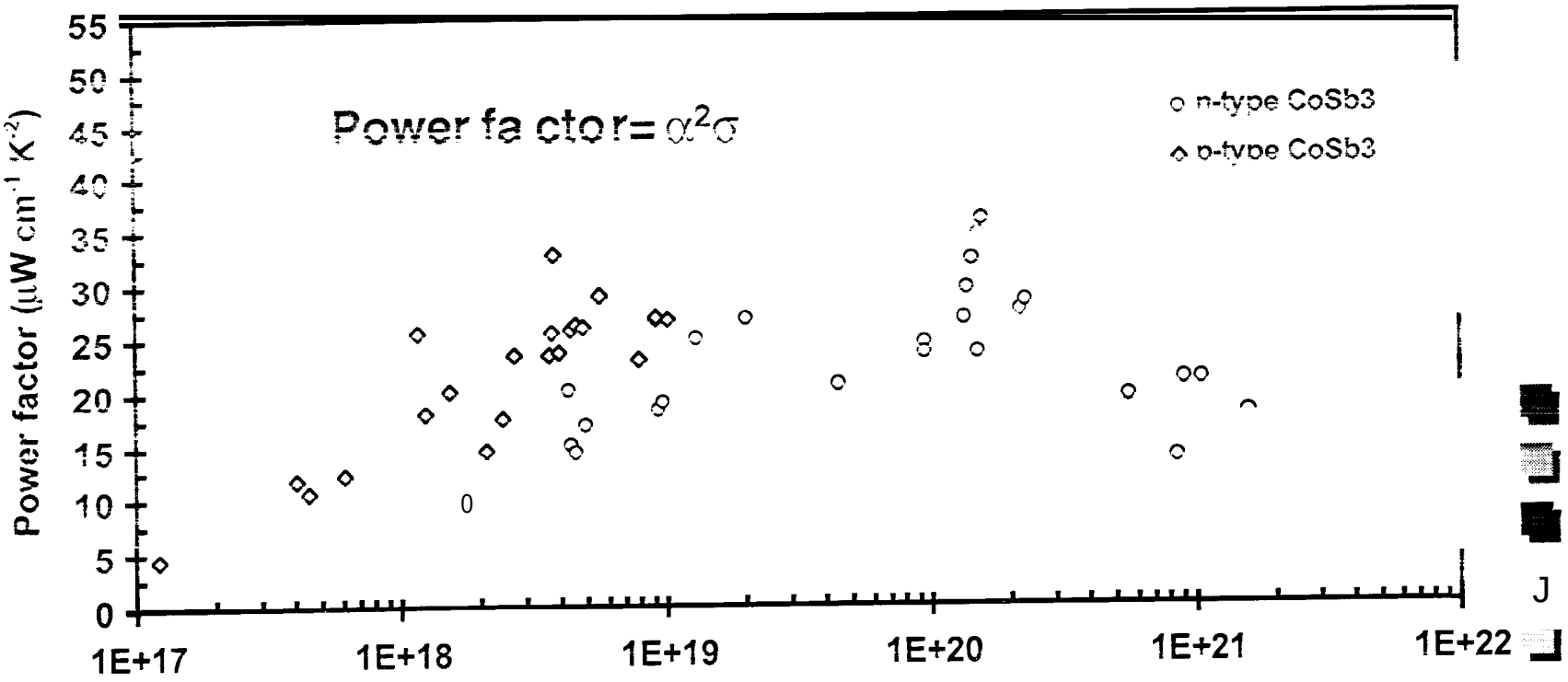
Binary Skutterudites: N-Type $CoSb_3$ Seebeck Coefficient vs. T



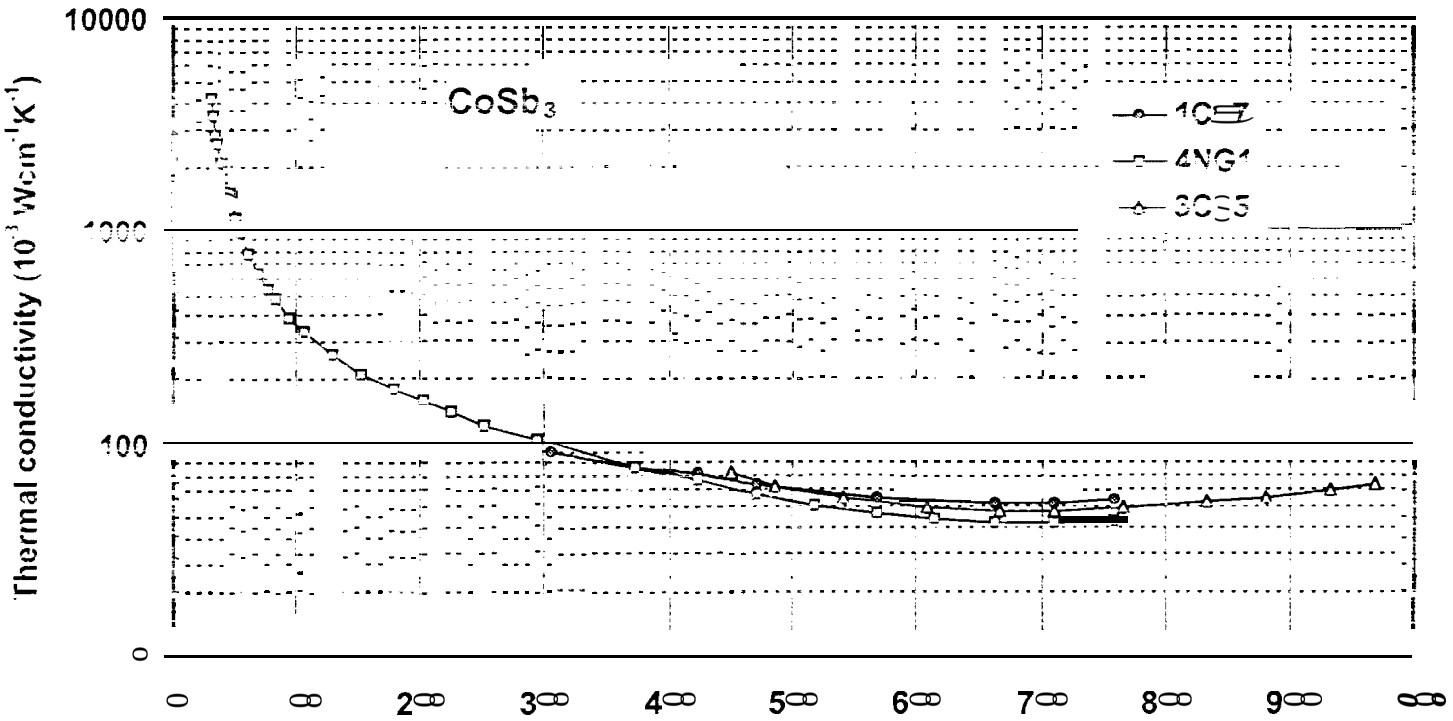
Binary Skutterudites: N-Type $CoSb_3$ Hall Mobility vs. T



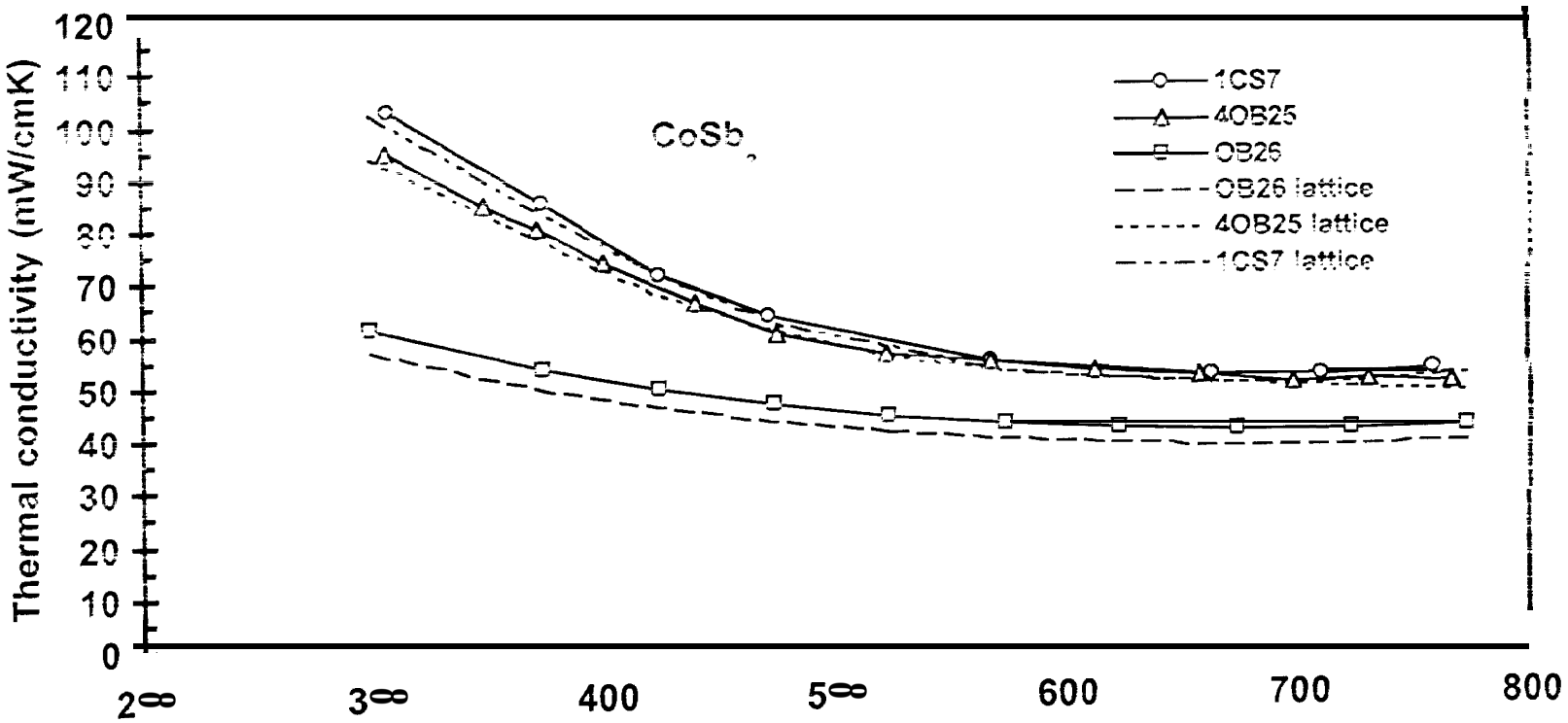
Power factor values for n- and p-type $CoSb_3$ at 300K



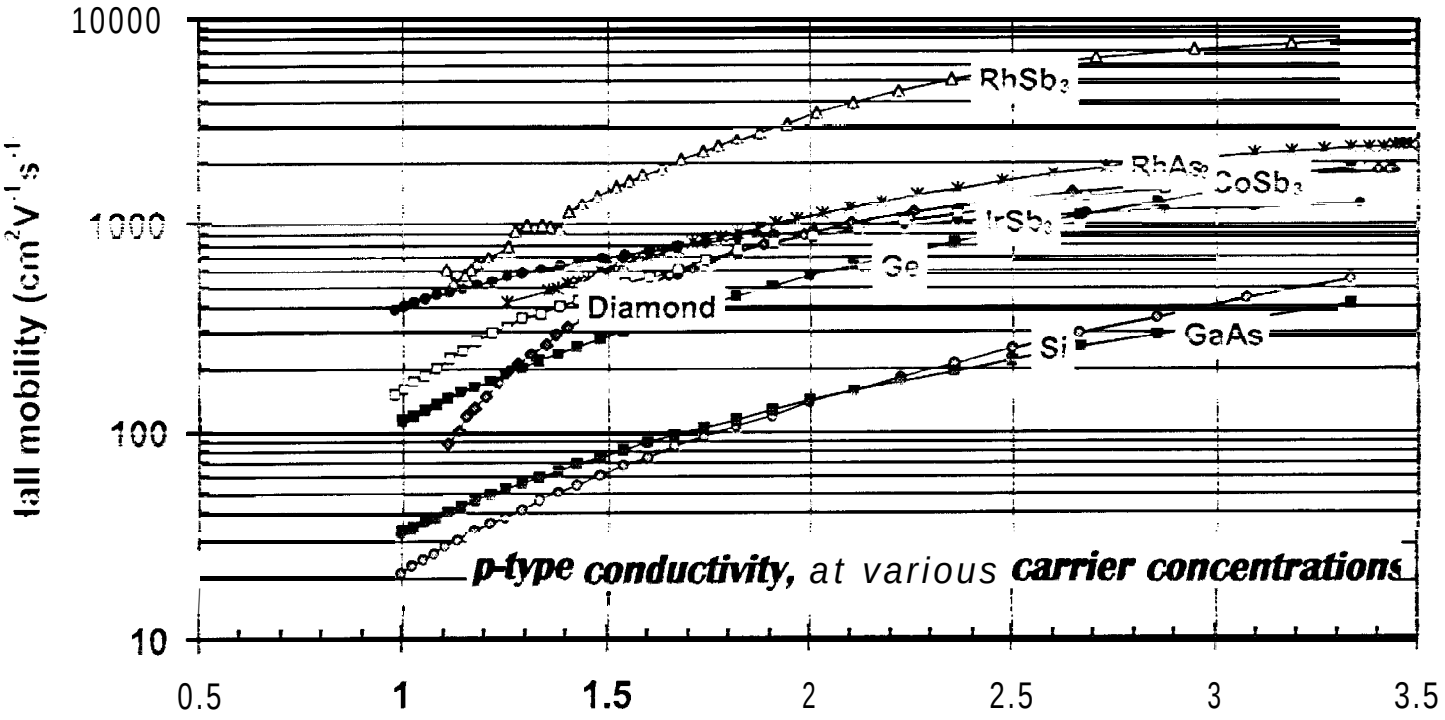
Binary Skutterudites: $CoSb_3$ Thermal Conductivity vs. T



Electron-phon scattering mechanism in heavily doped n-type $CoSb_3$



Binary Skutterudites Hall Mobility vs. T



Summary on Binary Skutterudites

- High temperature band gap values: 0.4 - 1.2 eV
  - **Possibility of $CoSb_3$, $IrSb_3$ being zero-band gap semiconductors**
  - **Possibility of unusual non-parabolicity for valence band**
- P-type electrical properties
  - **Very high mobilities, low electrical resistivities**
    - Due to small effective masses (~ 0.1 m_o)
  - **Moderate p-type Seebeck coefficients (100-200 $\mu V.K^{-1}$)**
- N-type electrical properties
  - **N-type mobilities are lower but still reasonable**
    - Due to large effective masses (~ 1.5 m_o)
  - **Large n-type values (200-600 $\mu V.K^{-1}$)**
- Thermal conductivities are moderate
  - **But too high for thermoelectric applications**
- Large family of isostructural semiconductors
  - **N-type skutterudites might result in higher T/E performance**

➠ **Need for reductions in lattice thermal conductivity**

Ternary Compounds and Phases Derived from Binary Skutterudites

New compounds/phases are derived from binary compounds

- By replacing the transition metal or the pnicogen or both elements
- By conserving the number of valence electrons

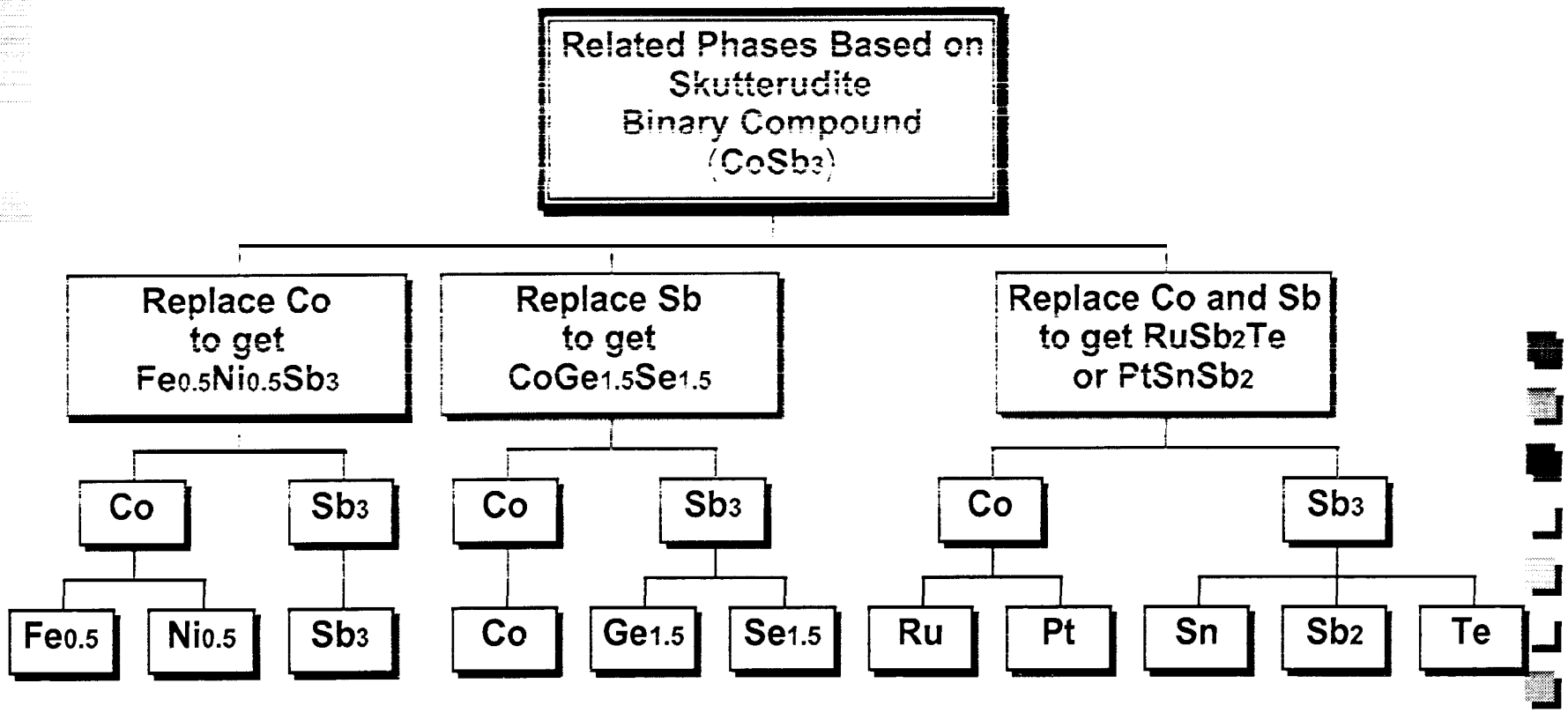
Our results (and literature data) show that numerous related skutterudite phases exist

- We know of 23 ternary phases (14 new ones found at JPL)

Transport properties can change dramatically

- Increased atomic disorder, changes in band structure, doping, and scattering mechanisms
- All new ternary compound characterized at JPL have low thermal conductivity (7 to 35 mW/cm.K)
- Each new phase should be separately characterized
- If promising, solid solutions are also considered

Ternary Compounds and Phases Derived from Binary Skutterudites



Ternary Skutterudite Phases

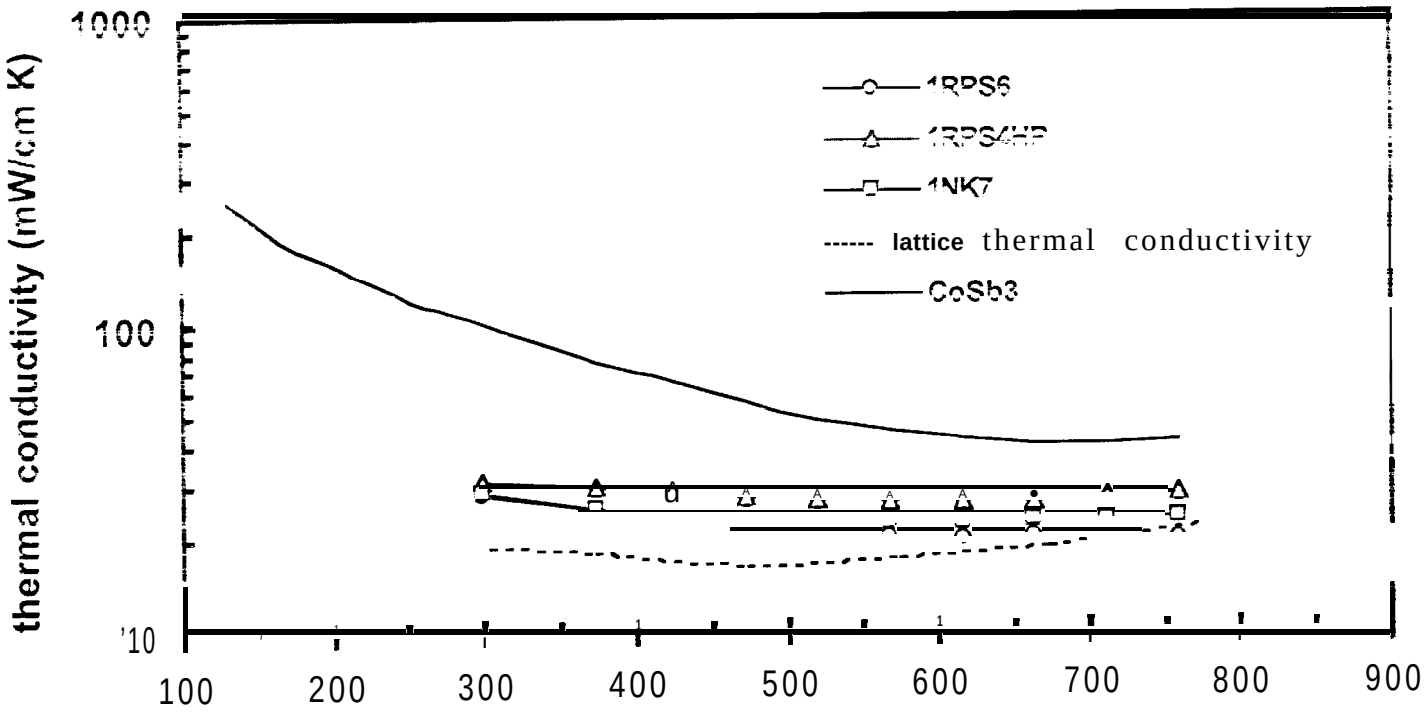
Compound	a (Å)	T_m (°C)
$CoGe_{1.5}S_{1.5}$	8.017	1000
$CoGe_{1.5}Se_{1.5}$*	8.299	800
[illegible]		> 800
[illegible]		
[illegible]	-	-
[illegible]	8.2746	> 800
$IrGe_{1.5}S_{1.5}$	8.297	> 800
[illegible]	8.5591	> 800
[illegible]	8.7050	> 800
[illegible]	-	-

* JPL findings

Compound	a (Å)	T_m (°C)	E_g (eV)
[illegible]	9.0904	729 *	~0.16*
[illegible]	9.2060*	-	-
[illegible]	9.1950*		-
[illegible]	9.1780*		-
[illegible]	9.2060*	647 *	~0.60*
[illegible]		-	-
[illegible]	9.256		-
[illegible]			-
$FeSb_2Te$*	9.112*	556*	~0.27*
[illegible]	9.257*	-	-
$RuSb_2Te$*	9.268*	810*	1.20*
[illegible]	9.298*	> 800	
[illegible]	9.390		
$NiGeP_2$*	7.9040		
[illegible]	9.440	-	-

* JPL findings

Lattice thermal conductivity reduction due to electron charge transfer in ternary compounds: $Ru_{0.5}Pd_{0.5}Sb_3$



Solid Solutions and Alloys Derived from Binary and Ternary Skutterudites

- To form solid solutions is a well known approach
  - **All state-of-the-art thermoelectric materials are solid solutions**
- Solid solutions exist between most binary skutterudites
  - $CoSb_3$-$IrSb_3$: $IrSb_3$:110 mW/cm.K; $Co_{0.12}Ir_{0.88}Sb_3$: 28 mW/cm.K
  - $CoAs_3$-$CoSb_3$; CoP_3-$CoAs_3$; $IrAs_3$-$IrSb_3$
- Found solid solutions exist in many other systems, such as:
  - **$CoSb_3$-$Ru_{0.5}Pd_{0.5}Sb_3$**
  - **$IrSb_3$-$RuSb_2Te$**
  - **$Fe_{0.5}Ni_{0.5}Sb_3$-$Ru_{0.5}Pd_{0.5}Sb_3$**
- Reductions in lattice thermal conductivity, carrier mobility
  - **Should only need a few selected compositions to predict ZT_{max}**
- N-type compositions are so promising
  - **Currently working on them**

Skutterudite Solid Solutions

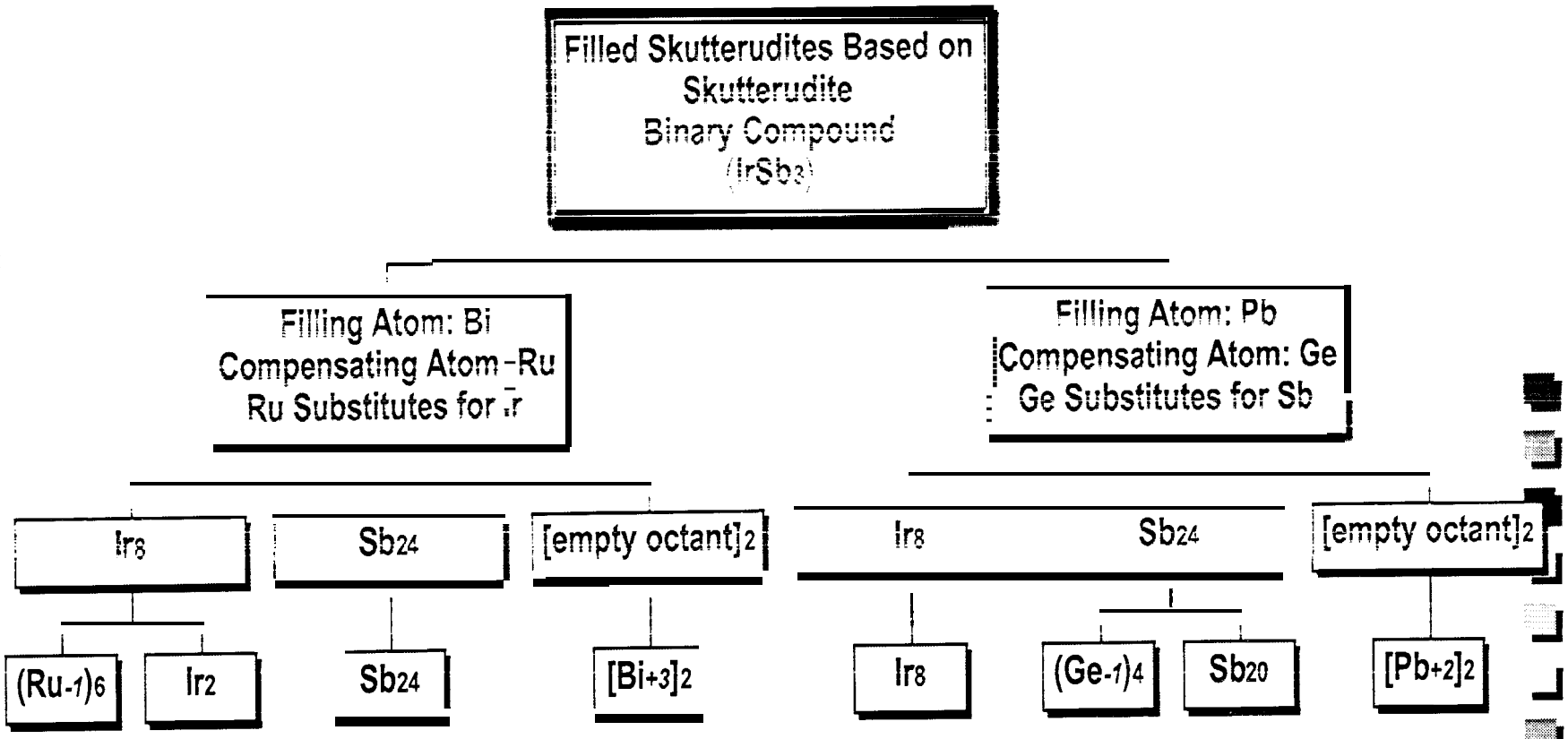
Solid Solutions	Partial Range of Compositions	Full Range of Compositions
CoP_3		$CoAs_3$*
$CoAs_3$	$CoSb_3$*, $IrAs_3$	
$CoSb_3$	$CoAs_3$*, $Fe_{0.5}Ni_{0.5}Sb_3$, $FeSb_2Te$, $FeSb_2Se$	$IrSb_3$
$RhSb_3$		$IrSb_3$
$IrAs_3$	$CoAs_3$, $IrSb_3$	
$IrSb_3$	$CoSb_3$, $IrAs_3$, $Fe_{0.5}Ni_{0.5}Sb_3$	$RhSb_3$, $RuSb_2Te$
$Fe_{0.5}Ni_{0.5}Sb_3$	$CoSb_3$, $IrSb_3$	$Ru_{0.5}Pd_{0.5}Sb_3$
$Ru_{0.5}Pd_{0.5}Sb_3$	$CoSb_3$, $IrSb_3$	$Fe_{0.5}Ni_{0.5}Sb_3$
$FeSb_2Te$	$CoSb_3$, $RuSb_2Te$	
$RuSb_2Te$	$FeSb_2Te$	$IrSb_3$

*literature results

Filled Skutterudites

- Literature data show that filled skutterudites can be formed
  - **Using rare earth elements such as La or Ce in a Fe_8P_{12} frame**
  - **But most of them were metallic**
- Preparation of filled skutterudites from binary compounds
  - **By filling the two empty octants present in the 32 atoms unit cell**
  - **With a heavy element such as Bi, Pb or Y**
  - **The number of valence electrons needs to remain constant to conserve a semiconducting behavior**
- Study compositions derived from filled skutterudites
  - **By substitution on the transition metal or pnicogen site**
  - **To compensate for the p-type metallic character**
- These approaches could substantially lower the lattice thermal conductivity values
  - **"rattling" atom in octant "cage"**
  - **Expect only slight reduction in carrier mobility**

Filled Skutterudites Derived from Binary Compounds



Results on Ternary Skutterudites, Alloys and Filled Skutterudites

Ternary skutterudites compounds

- **Most are p-type semiconductors**
  - **With high carrier concentrations**
- **Reasonably good Hall mobilities**
- **Moderate to low p-type Seebeck coefficients (100-200 $\mu V.K^{-1}$)**
- **Surprisingly low thermal conductivity**
  - **Cannot be explained from point defect scattering (compared to binaries)**
    Other phonon scattering mechanisms at work
    Such as valence fluctuations, charge exchanges

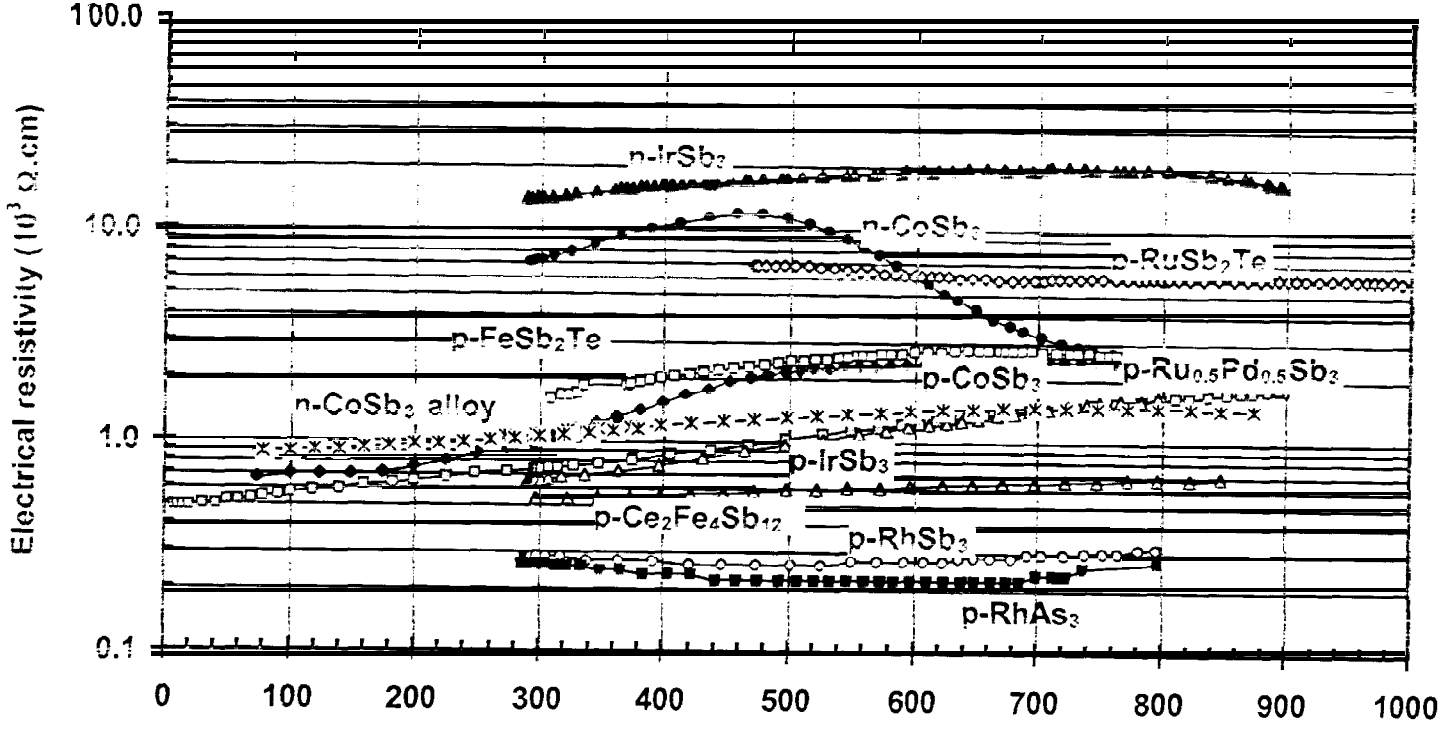
Skutterudite alloys

- **Both p-type and n-type can be obtained**
- **Goal is to maximize mass and volume fluctuations**

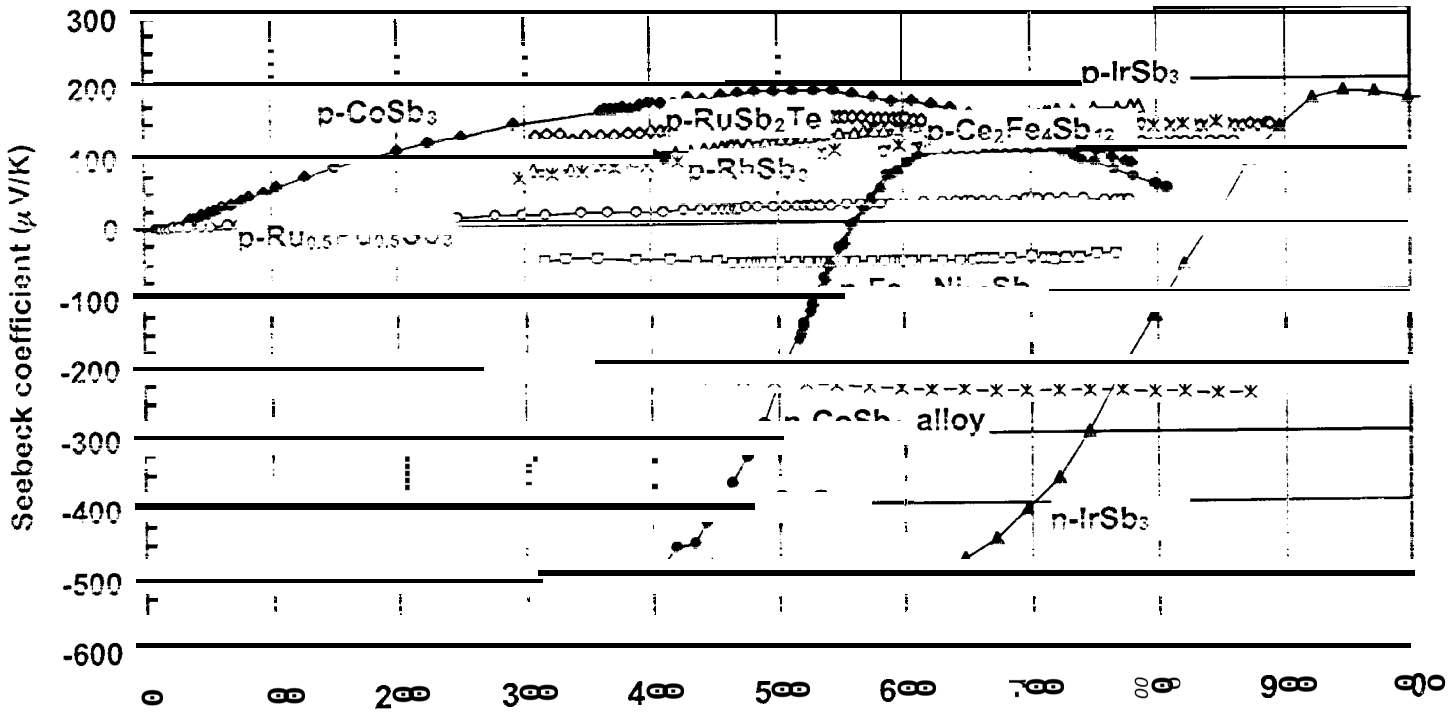
Filled skutterudites

- **Preliminary results indicate interesting thermoelectric properties**
- **Metallic behavior, but low thermal conductivity and good Seebeck**

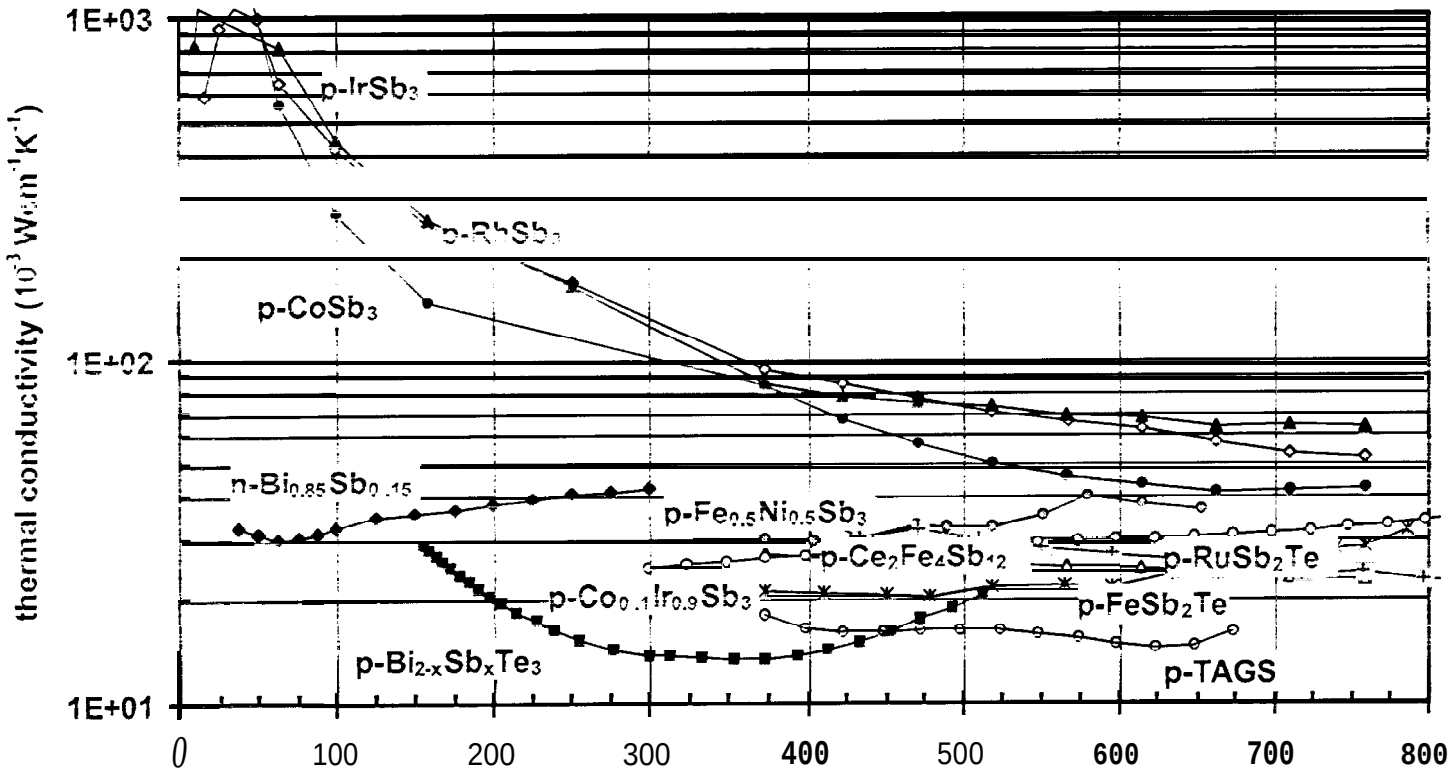
Electrical Resistivity of Skutterudites



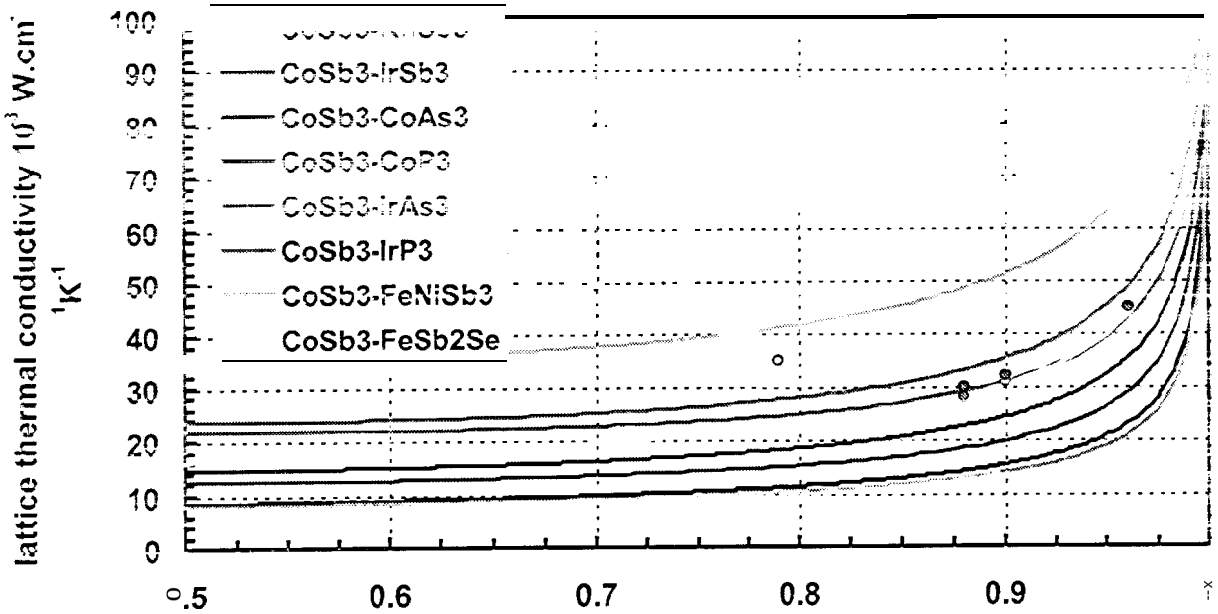
Seebeck Coefficient of Skutterudites



Thermal Conductivity of Skutterudites



Skutterudite Solid Solutions: Thermal Conductivity Reductions (calculated)



Current Focus of JPL Programs

- Understand variations of general properties of skutterudites
  - With composition
  - With doping level and temperature
- Focus is on ternary skutterudites and related phases
  - Remaining binary compounds (mostly phosphides) difficult to prepare
  - Thermal conductivity of binary skutterudites too high
  - Thermal conductivity of ternary compounds and alloys much lower
- Study of n-type materials of particular interest
  - Because of their large Seebeck
  - But requires high doping levels
- Study of filled skutterudites also promising
  - Because of their low thermal conductivity
  - Approach can be combined with alloys

Conclusion

- Exploratory search at JPL for new high performance thermoelectric materials identified skutterudite family
  - Skutterudites might also be of interest for electronics, other applications
- Several skutterudites have shown very interesting properties
  - Very low thermal conductivity semiconductors
  - Very high p-type mobility values
  - Large n-type Seebeck values
  - Large number of isostructural materials
- Systematic investigation of skutterudites
  - Necessary to understand trends in properties
  - Goal is to determine best approach for high ZT