# The Thermoelectrics of Bulk Materials: A History

Glen A. Slack

July 21, 2011

International Thermoelectric Society

Traverse City, Michigan

1 - NEW

## My Thanks to Coworkers

(alphabetical)

1) **Robert Berman-** Oxford University

2) **Christia Cros-** C.N.R.S., Bordeaux

3) **Julian Goldsmid-** University of Tasmania

4) **Frank Ham-** General Electric R & D Center

5) **Paul G. Klemens-** University of Connecticut

6) **Gerald D. Mahan-** Pennsylvania State University

7) **Donald t. Morelli-** Michigan State University

8) **George S. Nolas-** University of South Florida *

9) **Robert O. Pohl-** Cornell University *

10) **Sandra B. Schujman-** Rensselaer Poly. Inst. *

11) **Igor Smirnov-** Ioffe Institute, Leningrad

12) **Terry M. Tritt-** Clemson University

13) **Cronin Vining-** General Electric

14) **General Electric R .& D. Center**

$$Z = S^2\sigma/\kappa$$

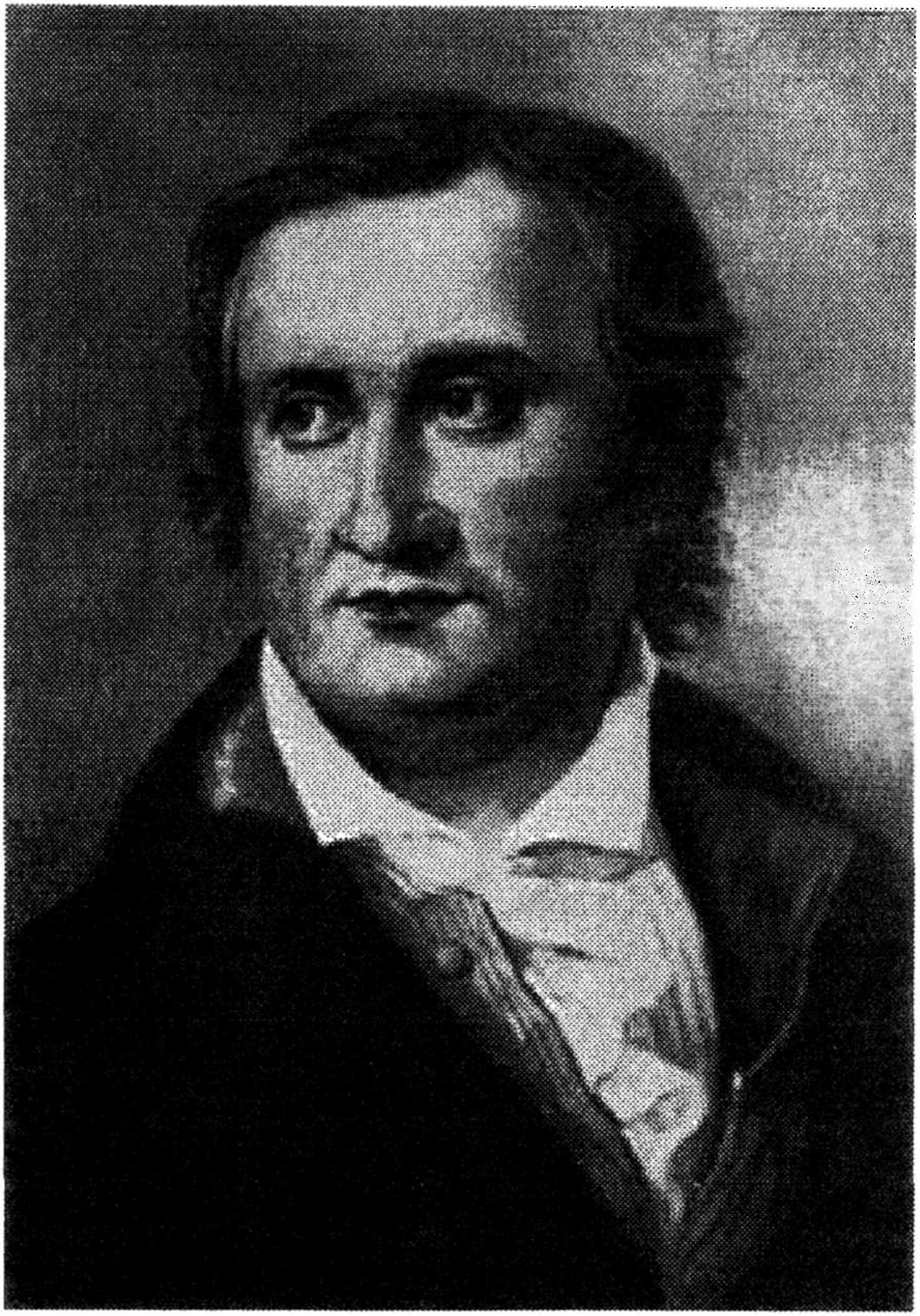
$$\kappa = \kappa_e + \kappa_p$$

**Important Historical Events**

**(1800 – 1900)**

1) **Alessandro Volta-** Italy- 1800- Voltaic pile
2) **Jean B.J. Fourier-** France-1812- defined thermal conductivity = K
3) **Hans Christian Orsted-** Denmark-1820- d.c. magnetic fields (used voltaic pile)
4) **Thomas Johann Seeback-** Prussia- 1822- thermoelectric voltage from 2 wires = S
5) **Sadi Carnot-** France- 1824- heat engine efficiency
6) **George S. Ohm**- Germany- 1827- defined and measured electrical conductivity = $\sigma$ (used thermopile)
7) **Jean C.A. Peltier**- France- 1834- d.c. current through a Bi-Sb junction ⇒ + Q (heat) ⇒ $\pi$
8) **James P. Joule**- England- 1843- d.c. current produces heat, $I^2R$
9) **William Thomson**- England- 1848- absolute zero is -273.1°C; 1857- reversible heat absorption by d.c. current "Thomson effect" = $\gamma$ (Lord Kelvin)
10) **E. Becquerel**- France- 1866- studied Zn-Sb and Cd-Sb thermoelectrics

# Thomas Johann Seebeck



**Born** 9 April 1770

Reval, Prussia

# Georg Simon Ohm

17 March 1789

Erlangen, Germany

# Jean Charles Athanase Peltier

Jean Charles Athanase Peltier, lithography by Antoine Maurin

| | |
|---|---|
| **Occupation** | Physicist |

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# MAGNETISCHE POLARISATION
der
# Metalle und Erze durch Temperatur-Differenz.

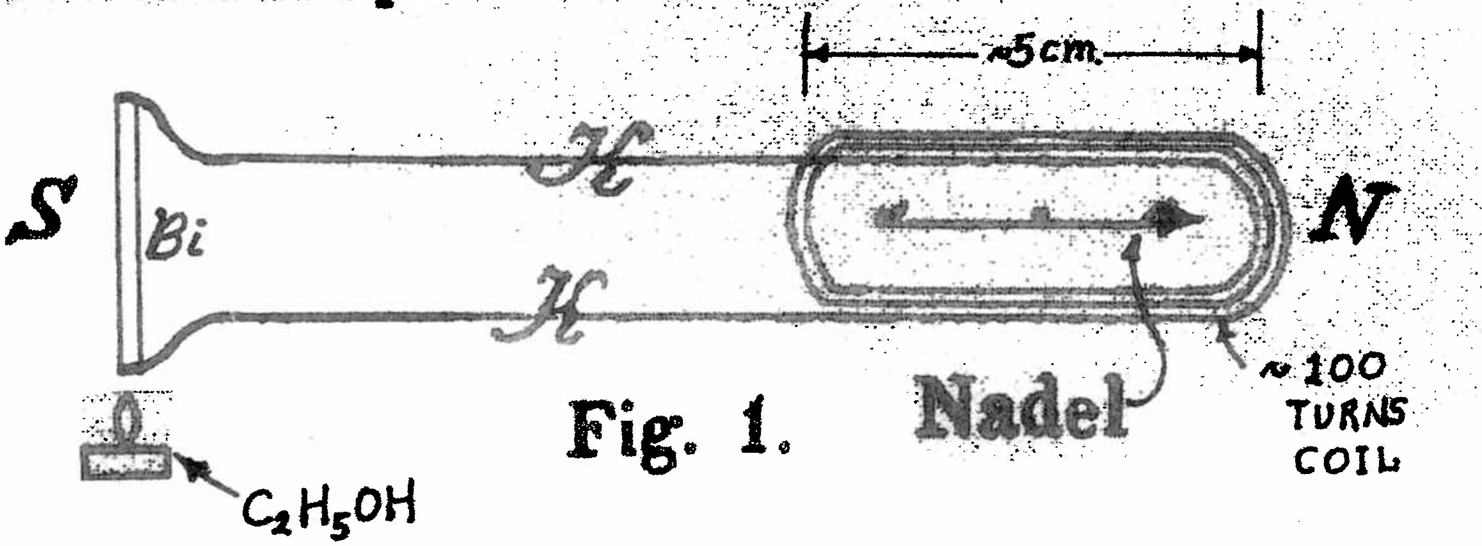



Fig. 1.

**Thomas Johann Seebeck, Abhandlung der Königlichen Preussischen Akademie der Wissenschaften zu Berlin,**

p265-375 (1822-1823)

**Seebeck Studied: 25 METALS, 30 minerals**

SOME METALS: Cu, Ag, Au, Pt, Hg, As, Bi, Sb, Te...

USEFUL MINERALS: PbS, $Bi_2S_3$, $CoAs_2$, $CuFeS_2$, FeAsS...

POOR MINERALS: ZnS, $Fe_2O_3$, $Al_2O_3$, $CuSO_4$, $TiO_2$, AgCl...

## 1851

# The Law of Magnus

The Seebeek voltage is independent of the temperature gradients along a homogeneous "wire" and depends only on the two junction temperatures.

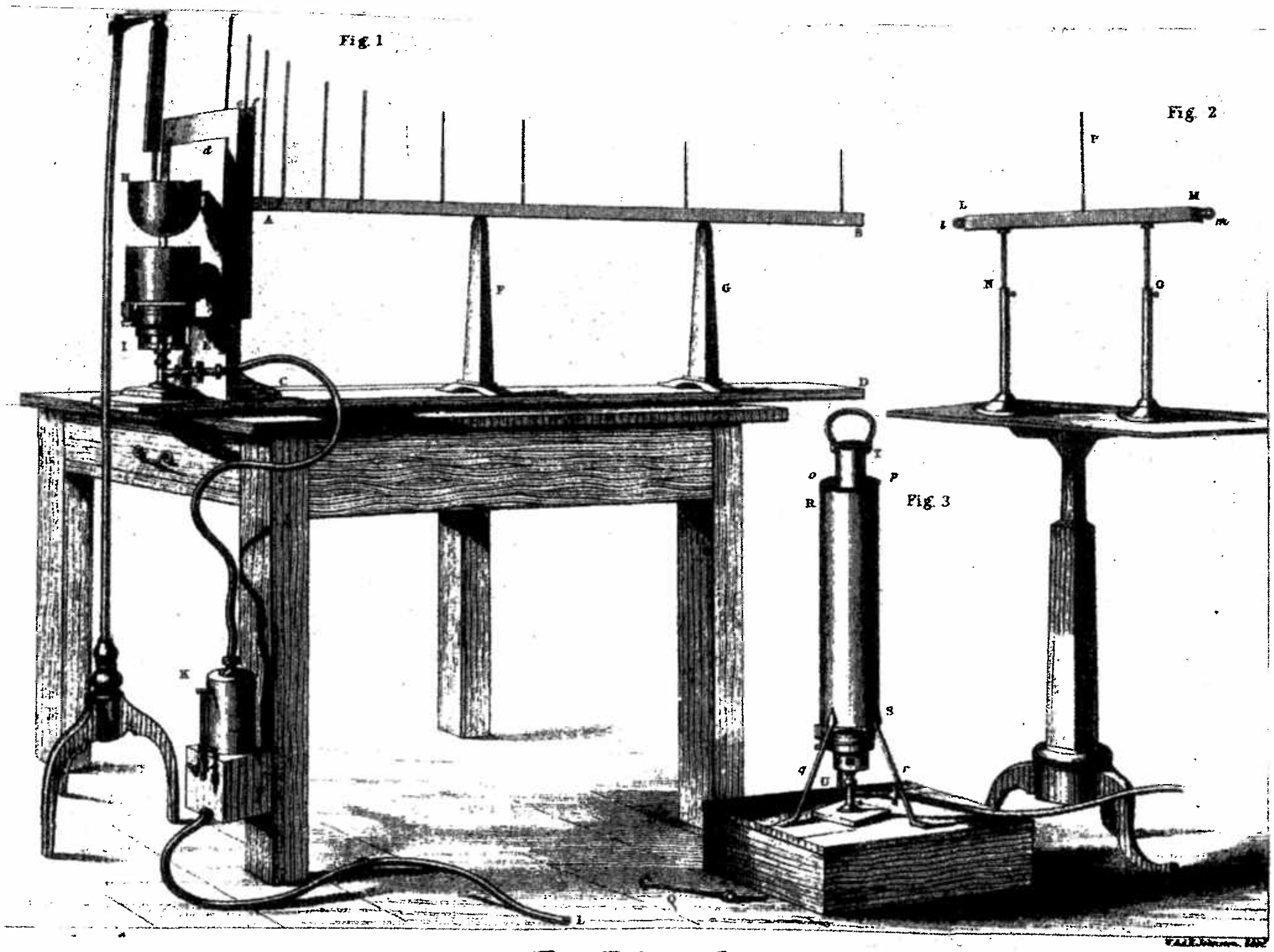
G. Magnus, Poggendorf's Annalen der Physik
83 469 (1851)

# James D. Forbes, LL.D.

Trans. Roy. Soc of Edinburgh 23, 133-146 (1861-4)

## *Experimental Inquiry into the Laws of the Conduction of Heat in Bars, and into the Conducting Power of Wrought Iron.*

XIII.—*Experimental Inquiry into the Laws of the Conduction of Heat in Bars, and into the Conducting Power of Wrought Iron.* By James D. Forbes, LL.D., D.C.L., F.R.S., V.P.R.S. Ed., Corresponding Member of the Institute of France, Principal of the United College of St Salvator and St Leonard, St Andrews.




FORBES

## "A Contribution to the Understanding of the Thermoelectric Properties of the Metal Alloys"

by **Werner Haken**, who worked under Rubens
(extracted from the Berlin Dissertation) Annalen der Physik, Vol.32: 291-336 (1910)

Earlier authors almost never studied thermoelectric compounds, only metal alloys. However, Becquerel studied ZnSb and CdSb. Results vs Copper:

| Compound | Microvolt/ °C | Melt °C |
|---|---|---|
| Sb | +32 | |
| $Bi_2Te_3$ | +138 | 573 |
| SnTe | +103 | 779 |
| $Sb_2Te_3$ | +82 | 629 |
| $Cu_3P$ | +6.9 | |
| $Ag_3Sb$ | -7.8 | |
| PbTe | -70 | 917 |
| 90Bi+10Sb | -78 | |
| Bi | -58 | |

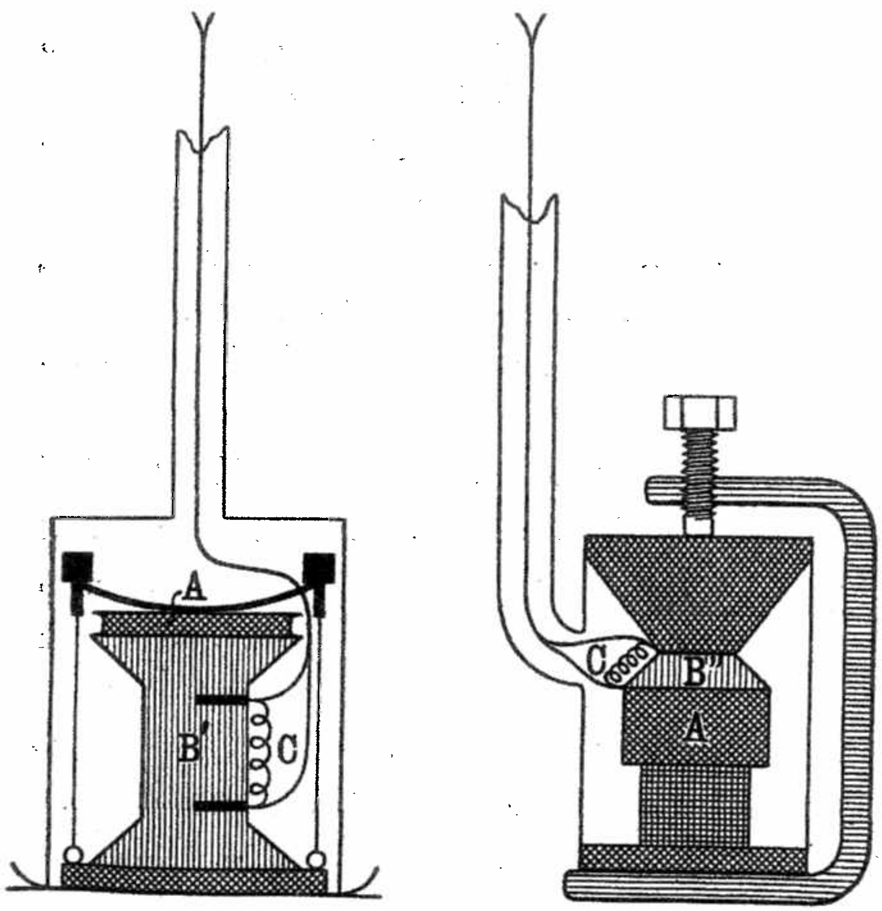
Conclusion: Metal alloys make better thermopiles than these compounds (because $\sigma$ is larger)

# Die Wärmeleitfähigkeit einiger Kristalle bei tiefen Temperaturen.

Von

A. Eucken.

Ann. d. Phys. (4) 34, 185, (1911)




I II

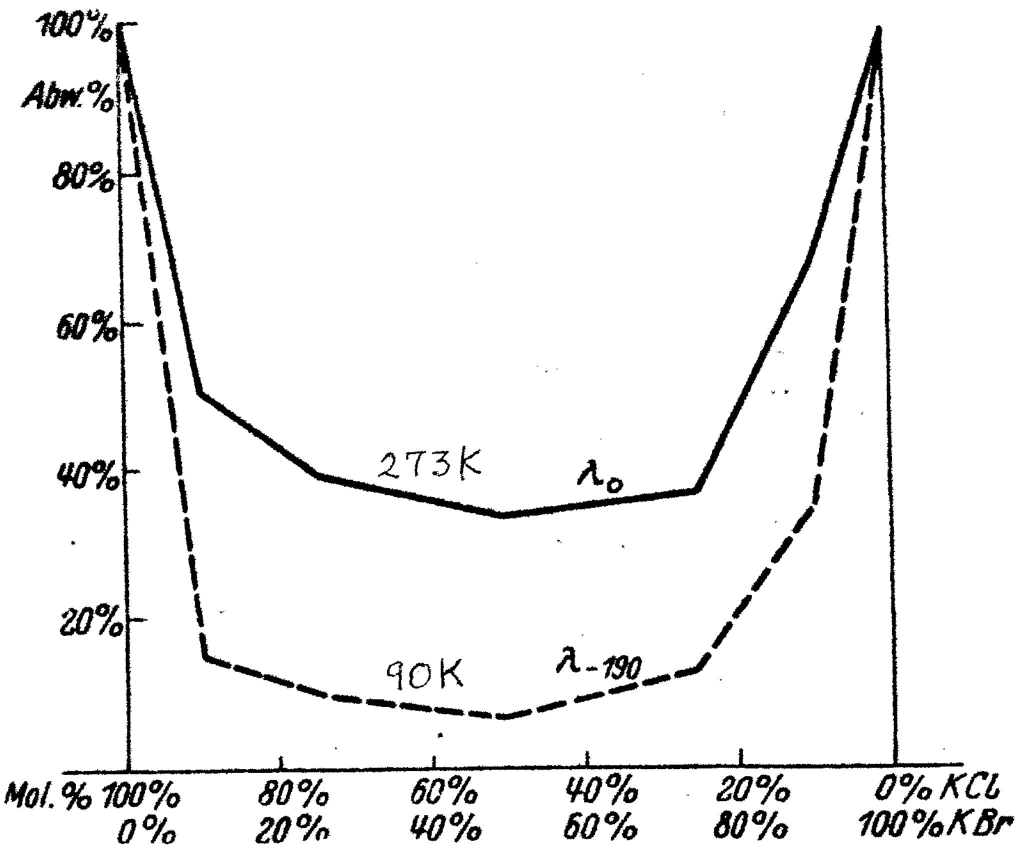
*A* Heizkörper, *B'* Körper aus Bergkristall, $SiO_2$
*B''* Diamantplatte, *C* Thermoelement.
Cu vs Cu-Ni

# Ergebnisse neuer Messungen der Wärmeleitfähigkeit fester krystallisierter Stoffe bei 0° und −190° C.

Von

**A. Eucken und G. Kuhn**

**Z. physikal. Chem. 134, 193 (1928)**




Abweichungen des Wärmeleitvermögens verschiedener *KCl*—*KBr*-Mischkristalle von den additiv zu berechnenden Werten.

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# THEORY

EUCKEN AND KUHN (1928)

**I.** ORDERED, PERIOIC MASS DIFFERENCE K (NaF)>K (NaI)

ACOUSTIC PHONON VELOCITY ↓

SMALL DECREASE IN $K_g$

**II.** RANDOM MASS DIFFERENCE

K(KBr)>> K ($KCl_{0.5}Br_{0.5}$)

PHONON M.F. PATH ↓

16B

# Thermoelectric Milestones (1900-2000)

1909 Altenkirch-- Calculated thermoelectric efficiency

1910 Haken-- PbTe and $Bi_2Te_3$, and Te are thermoelectrics

1911 Eucken-- Measured crystal $K_g$ with thermocouples

1914 Debye-- $K_g$ related to $C_v$

1928 Strutt-- Electron band theory of crystals

1928 Eucken and Kuhn-- Mass fluctuation $\downarrow K_g$

1957 Ioffe-- Thermoelectric book

1957 Dudkin and Abrikosov--$CoSb_3$ is a thermoelectric

1979 Slack-- Concept of MINIMUM $K_g$

1982 Ross and Anderson--"rattlers" in ice $\downarrow K_g$

1994 Slack-- Concept of "PGEC"

1995 Nolas, Slack, Tritt, and Morelli--"Rattlers" in skutterudites and $K_g \downarrow$

GENERAL ELECTRIC
Research Laboratory
SCHENECTADY, NEW YORK

# EFFECT OF ISOTOPES ON LOW-TEMPERATURE THERMAL CONDUCTIVITY

BY

GLEN A. SLACK

Physical Review, Vol. 105, No. 3, 829–831, February 1, 1957

"The experimental results on single crystals of Si, Ge, and KCl indicate that their maximum thermal conductivities are limited by isotope scattering of phonons rather than phonon-phonon scattering."

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PHYSICAL REVIEW, Vol. 110, No. 3, 773–775, May 1, 1958

# Isotopic and Other Types of Thermal Resistance in Germanium*

T. H. GEBALLE AND G. W. HULL
*Bell Telephone Laboratories, Murray Hill, New Jersey*
(Received March 10, 1958)

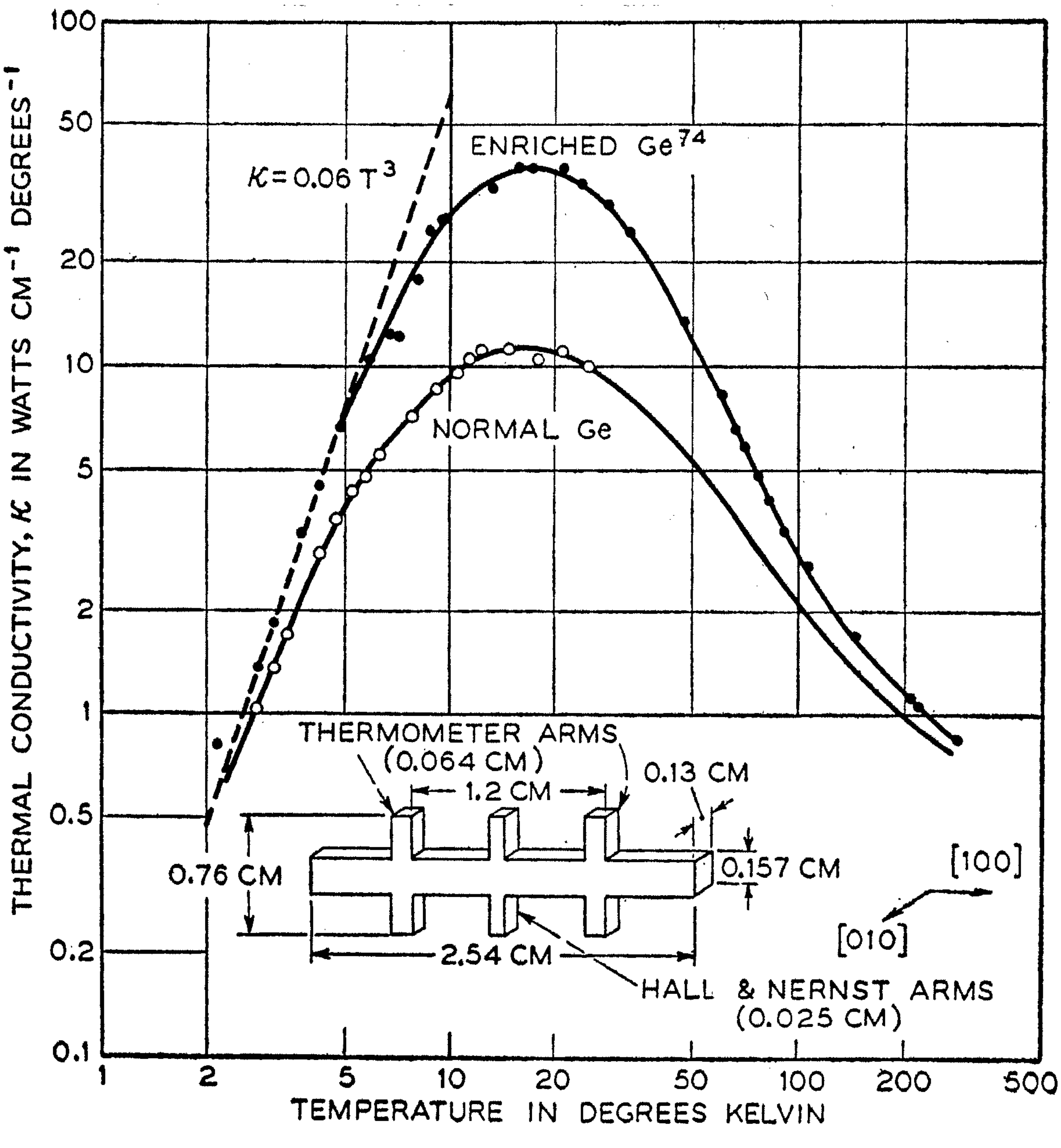


FIG. 1. Isotope effect on thermal conduction in Ge.

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# REDUCING $K_g$

**Lattice Effects**

**Other phonons**
**Isotopes**
**Vacancies**

**Atom transitions between 2 equal sites (flip-flop)**

**Internal molecular rotations ($NH_4Cl$, $CH_4$)**

**Rattle of atoms in cages (clathrates)**

**Converson of acoustic phonons to optic phonons (change crystal structure)**

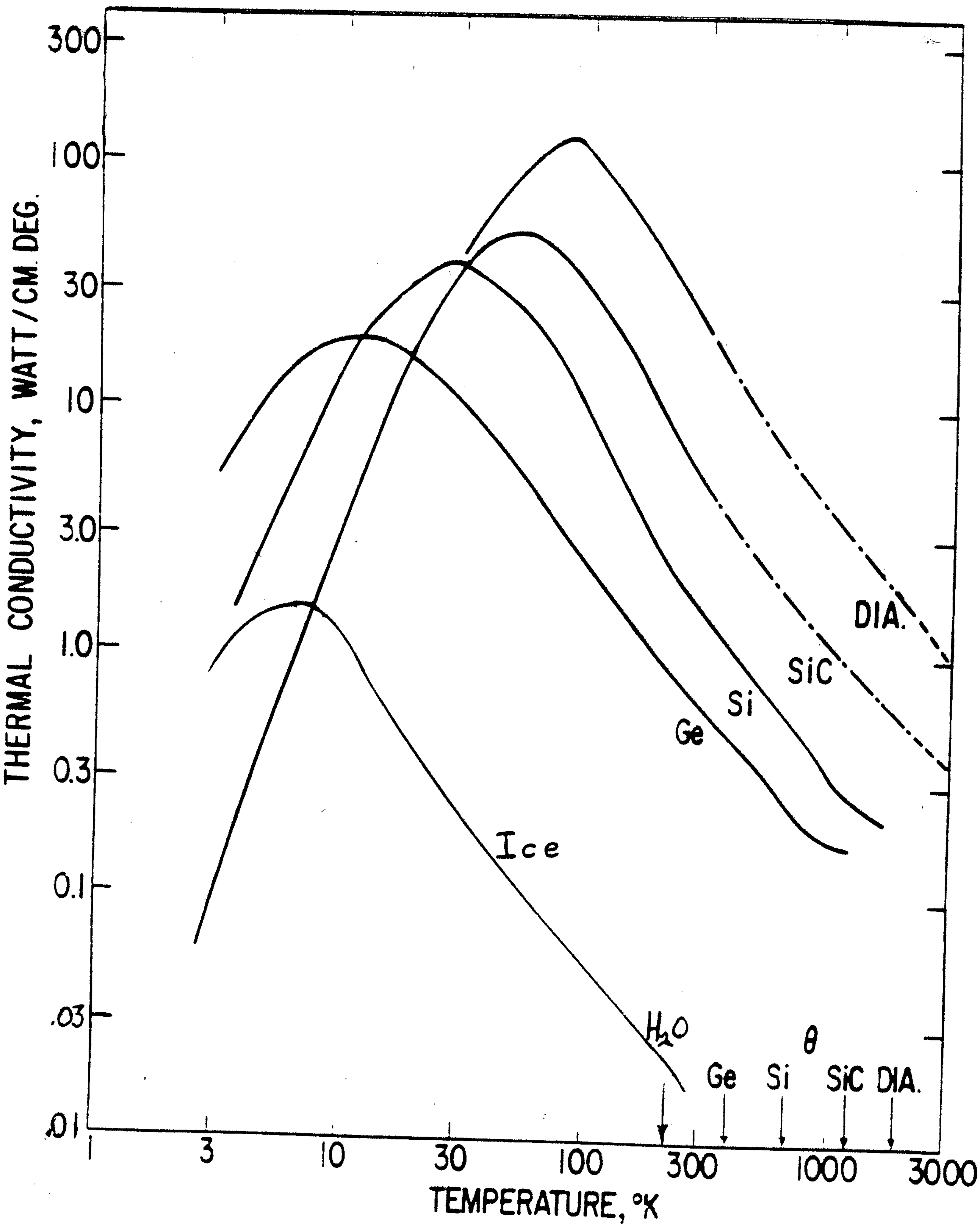
**Electron effects**

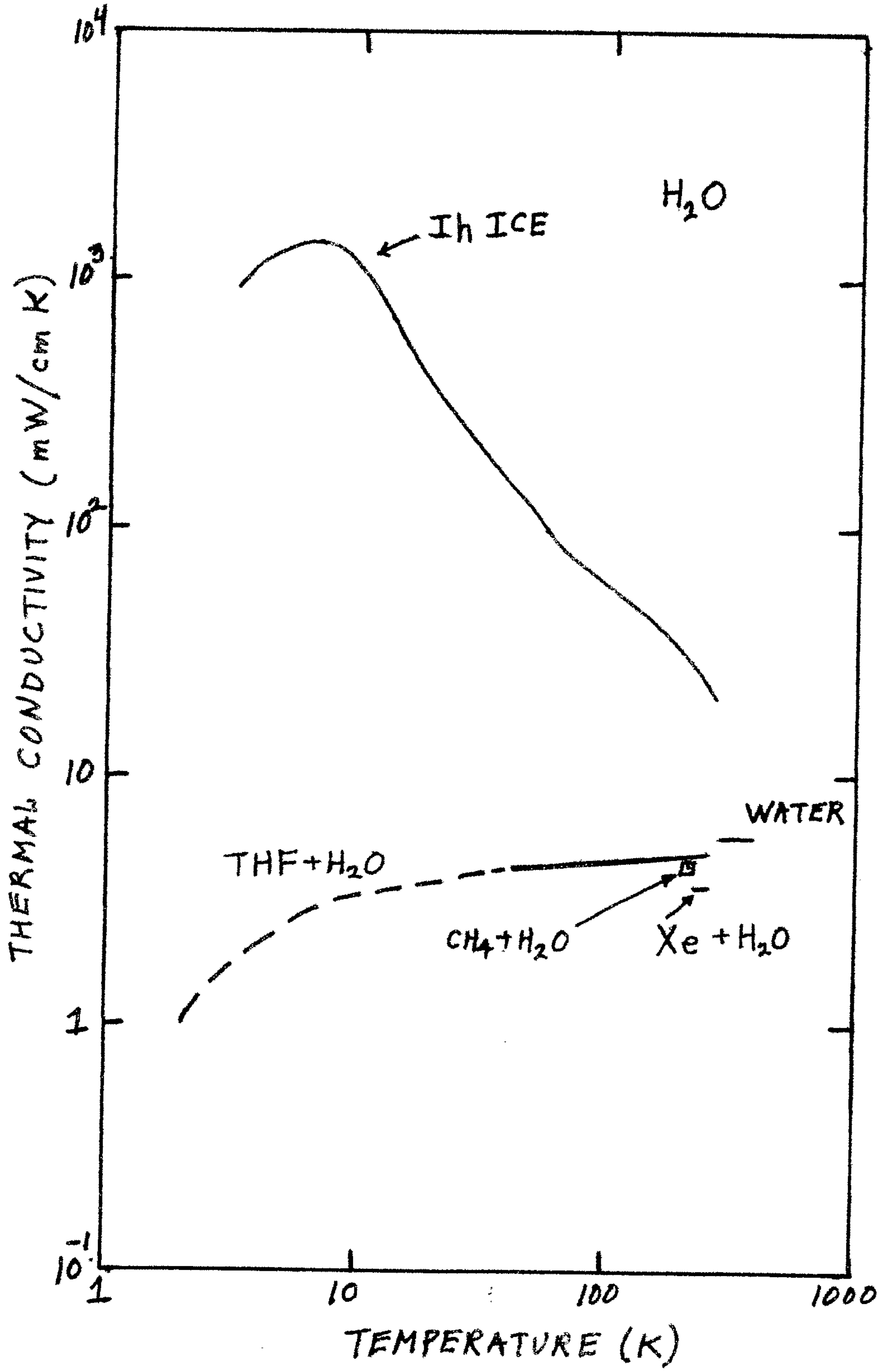
**Bound electron spin disorder (antiferromagnets)**

**Free electrons (donors or acceptors)**

**Valence fluctuations ($Fe_3$ $O_4$)**

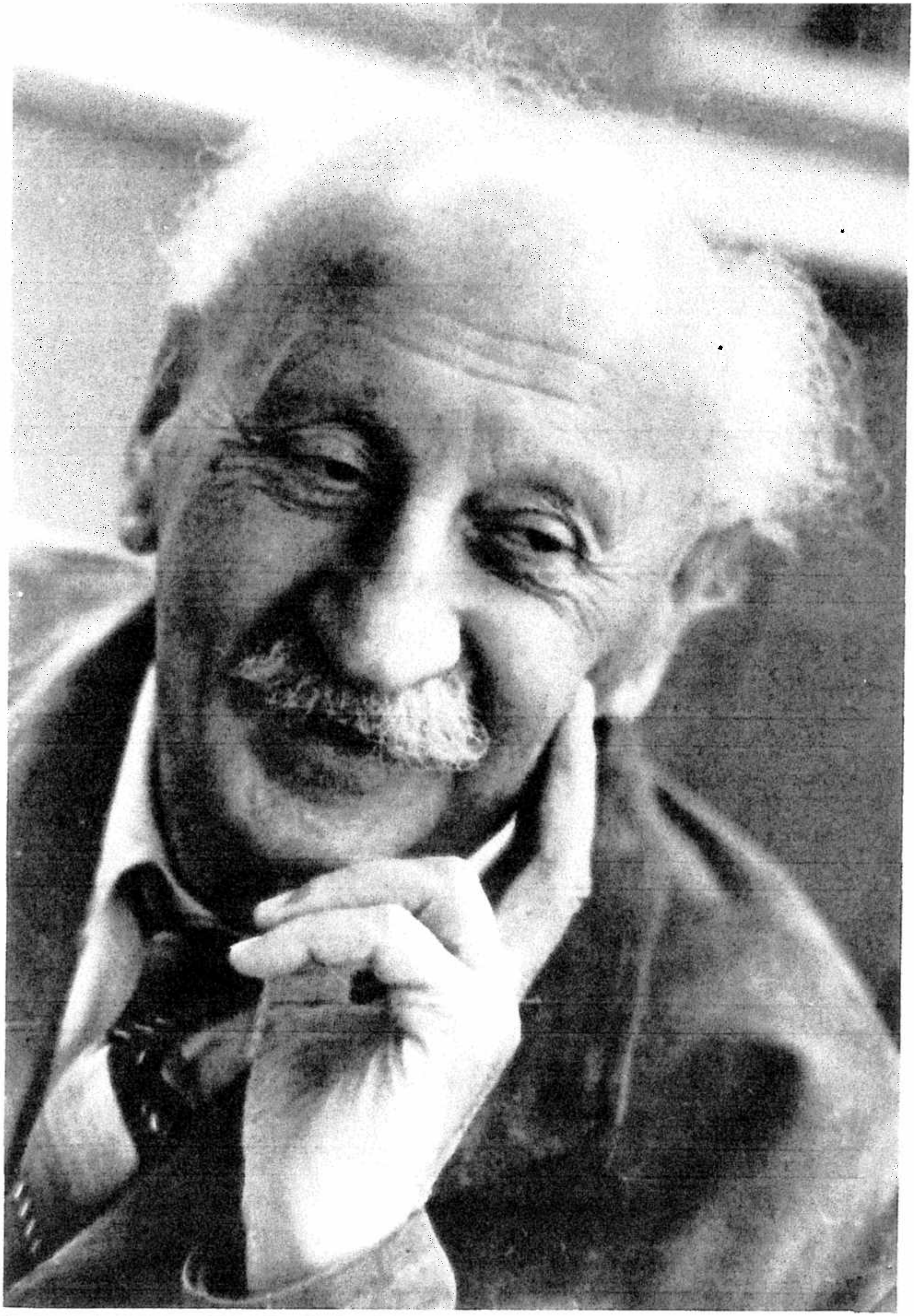
**Electron transitions within d- or f-shells**


THERMAL CONDUCTIVITY, WATT/CM. DEG.
300
100
30
10
3.0
1.0
0.3
0.1
.03
.01
1
3
10
30
100
300
1000
3000
TEMPERATURE, °K
DIA.
SiC
Si
Ge
Ice
H2O
θ
Ge
Si
SiC
DIA.




ICE: G.A. Slack, Phys. Rev. B22, 3065-3071 (1980)

THF in ICE: R.G. Ross and P. Andersson, Canadian Journal of Chemistry 60, 881-892 (1982)



Ioffe

Soviet Physics
# SOLID STATE
*A Translation of the Journal "Fizika Tverdogo Tela"*
(Russian Original Vol. 2, No. 5, pp. 781-1032, May, 1960)

Vol. 2, No. 5, pp. 719-932 November, 1960

## THERMAL CONDUCTIVITY OF SEMICONDUCTOR SOLID SOLUTIONS

A. V. Ioffe and A. F. Ioffe

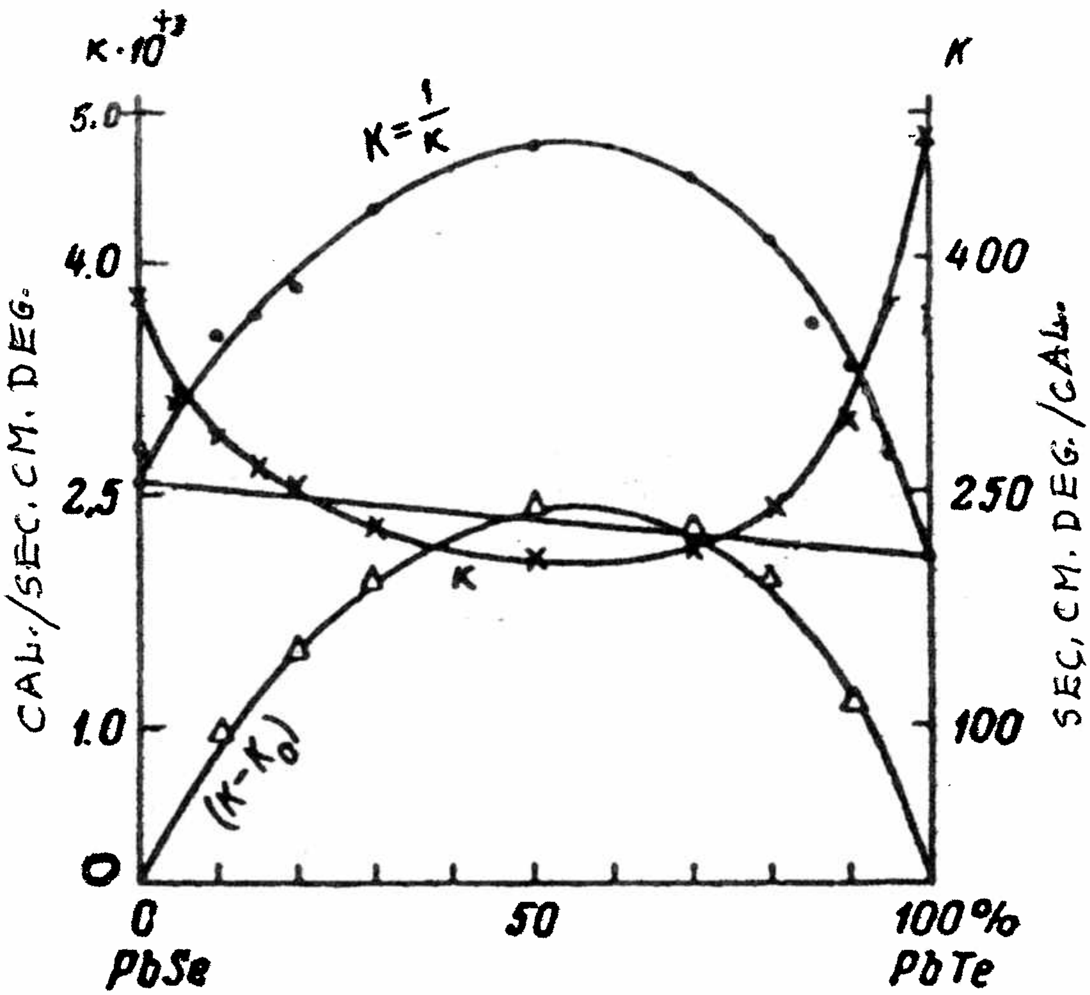



Fig. 7. (280K)

# CONTRIBUTIONS OF IOFFE

1. BUILT IOFFE INSTITUTE, LENINGRAD

2. BUILT PbS THERMO-GENERATORS CIRCA 1942-1945 (BASED ON SEEBECK'S DATA)

3. RENEWED WORLD INTEREST IN THERMOELECTRICS 1950-1965

4. PROMOTED (BUT DID NOT INVENT) PbSe, PbTe , $Sb_2Te_3$, $Bi_2Te_3$, Pb[Te-Se]

5. Prague, 1960

26B

# The Thermal Conductivity of Nonmetallic Crystals

GLEN A. SLACK

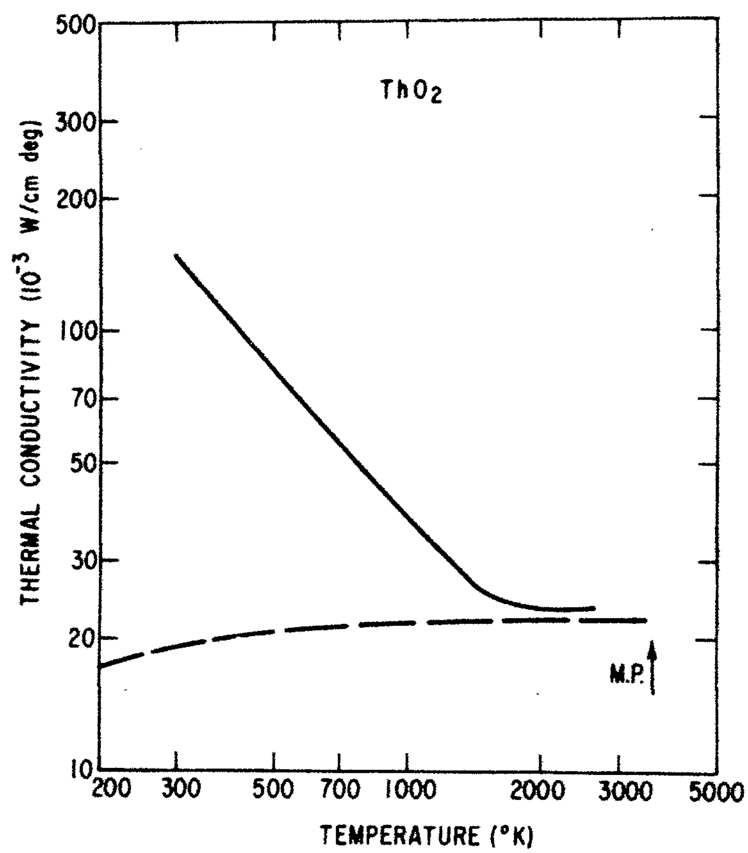
*General Electric Research and Development Center, Schenectady, New York*

SOLID STATE PHYSICS, VOL. 34, 1-71 (1979)

## Absolute Value of the Thermal Conductivity

$$K(T) = B\bar{M}\delta(\theta_0)^3 n^{-2/3} T^{-1}(\gamma)^{-2}$$

## Minimum Thermal Conductivity




m.f.p = λ

FIG. 18. The thermal conductivity versus temperature for $ThO_2$ up to the melting point. The measured value (—) approaches the calculated minimum (---) above 1700°K.

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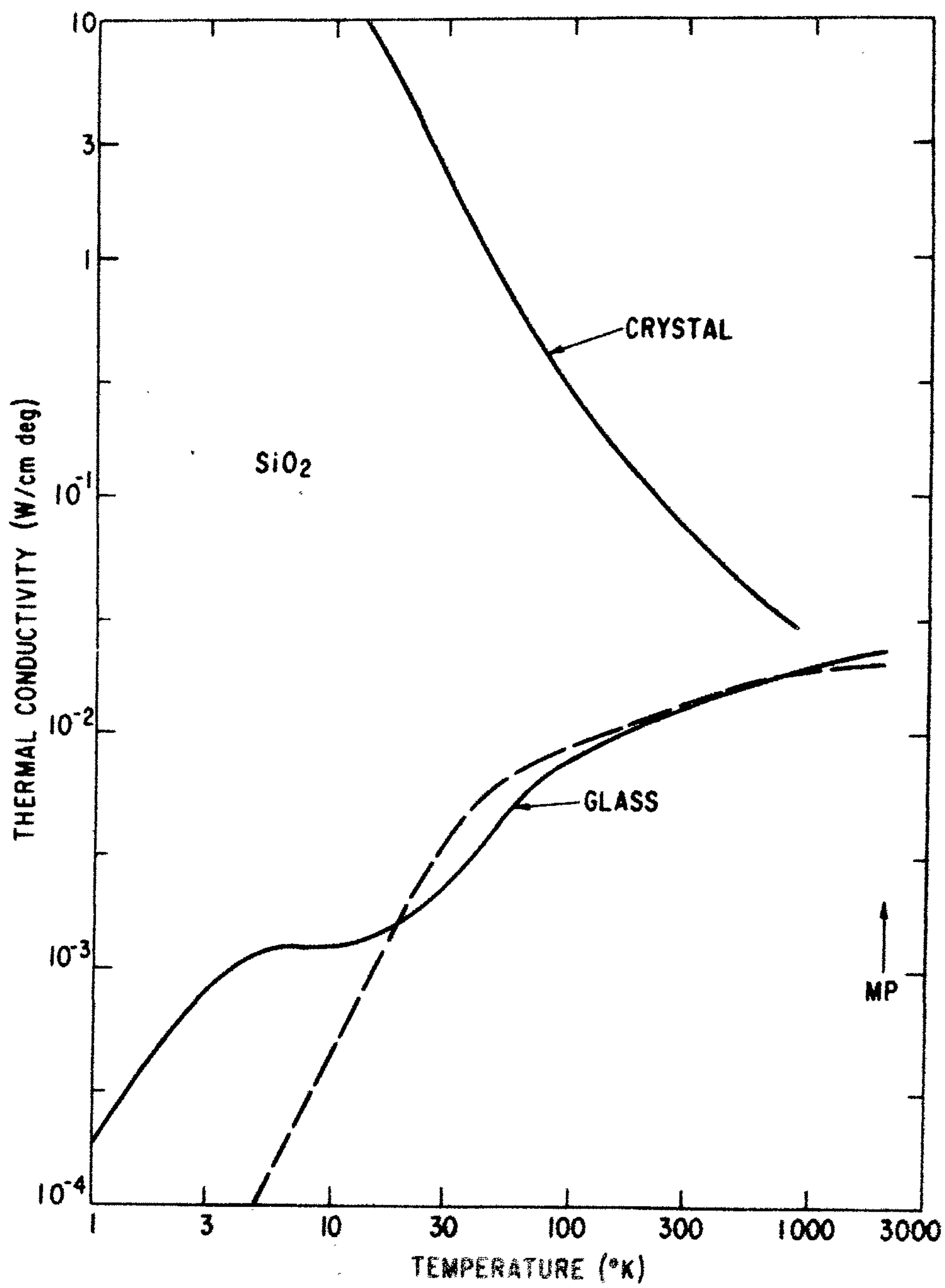
# Minimum Thermal Conductivity

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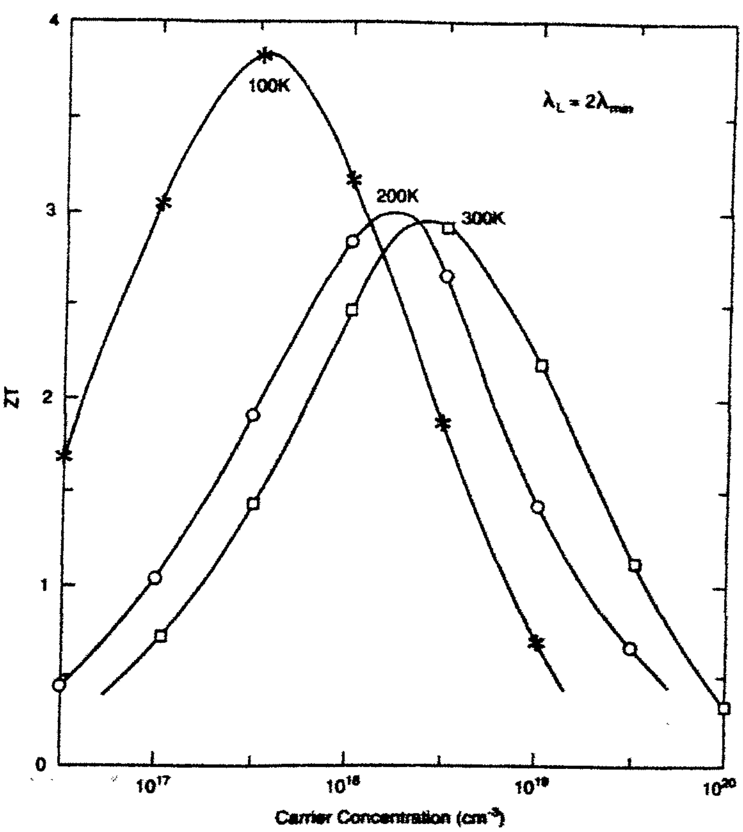
# New Materials and Performance Limits for Thermoelectric Cooling

Glen A. Slack
*Rensselaer Polytechnic Institute*
*Troy, New York, U.S.A.*

CRC handbook of thermoelectrics / edited by D. M. Rowe
1994

## PGEC

a phonon glass and an electron single crystal




**ZT, vs. carrier concentration**

## $IrSb_3$ *

Reasons chosen:

1. It is a semiconductor (not metal) (Dudkin and Abrikosov, 1956)
2. Band-gap 1.4eV
3. Stable to 1100°C
4. Heavy atoms⇒ Low $K_g$
5. Small electonegativity difference, 0.10
6. Cubic
7. Lattice voids⇒doping benefit
8. "Rattling" Atoms came later

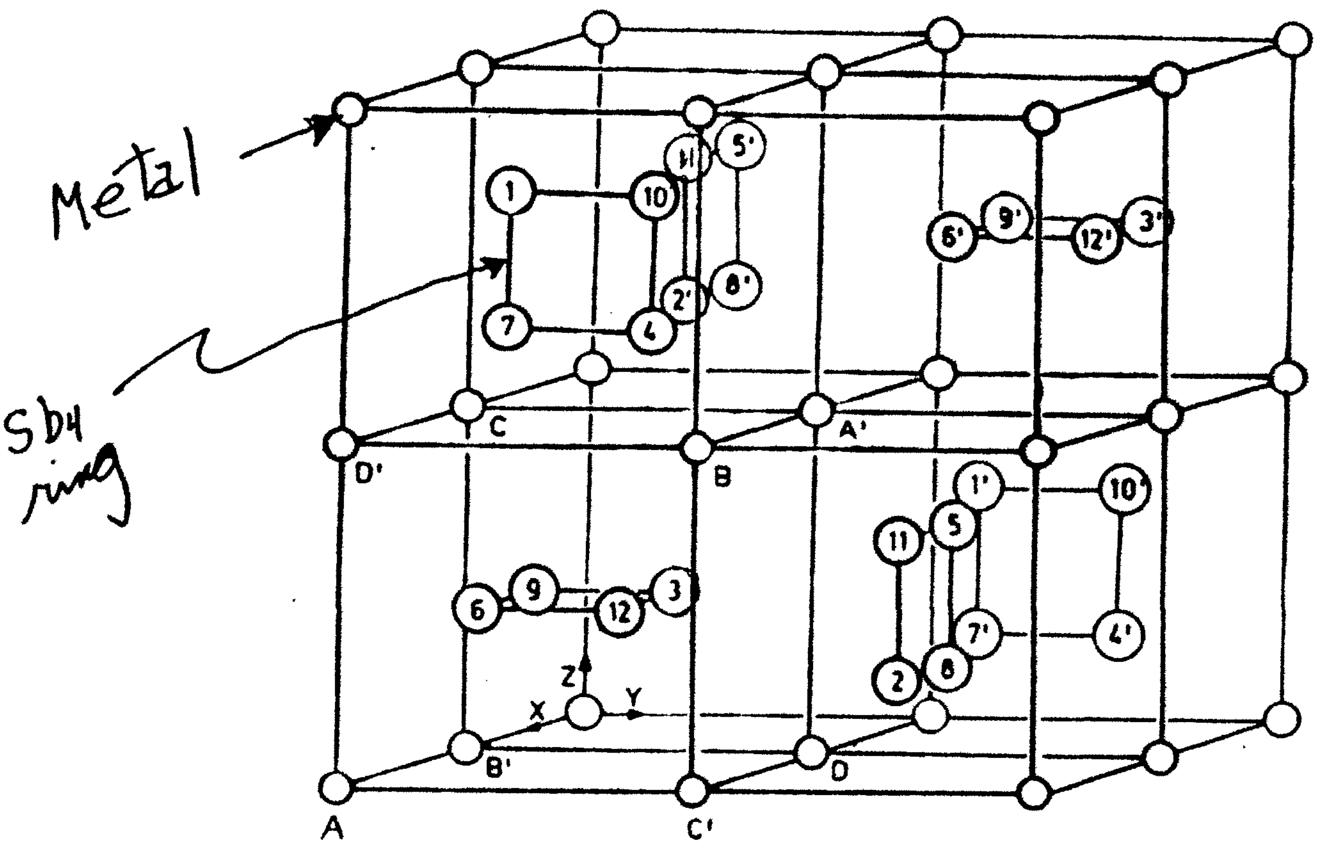
*Work stated at G.E., Feb. 1988

First Published Paper 1994

# TWO KINDS OF CRYSTALS

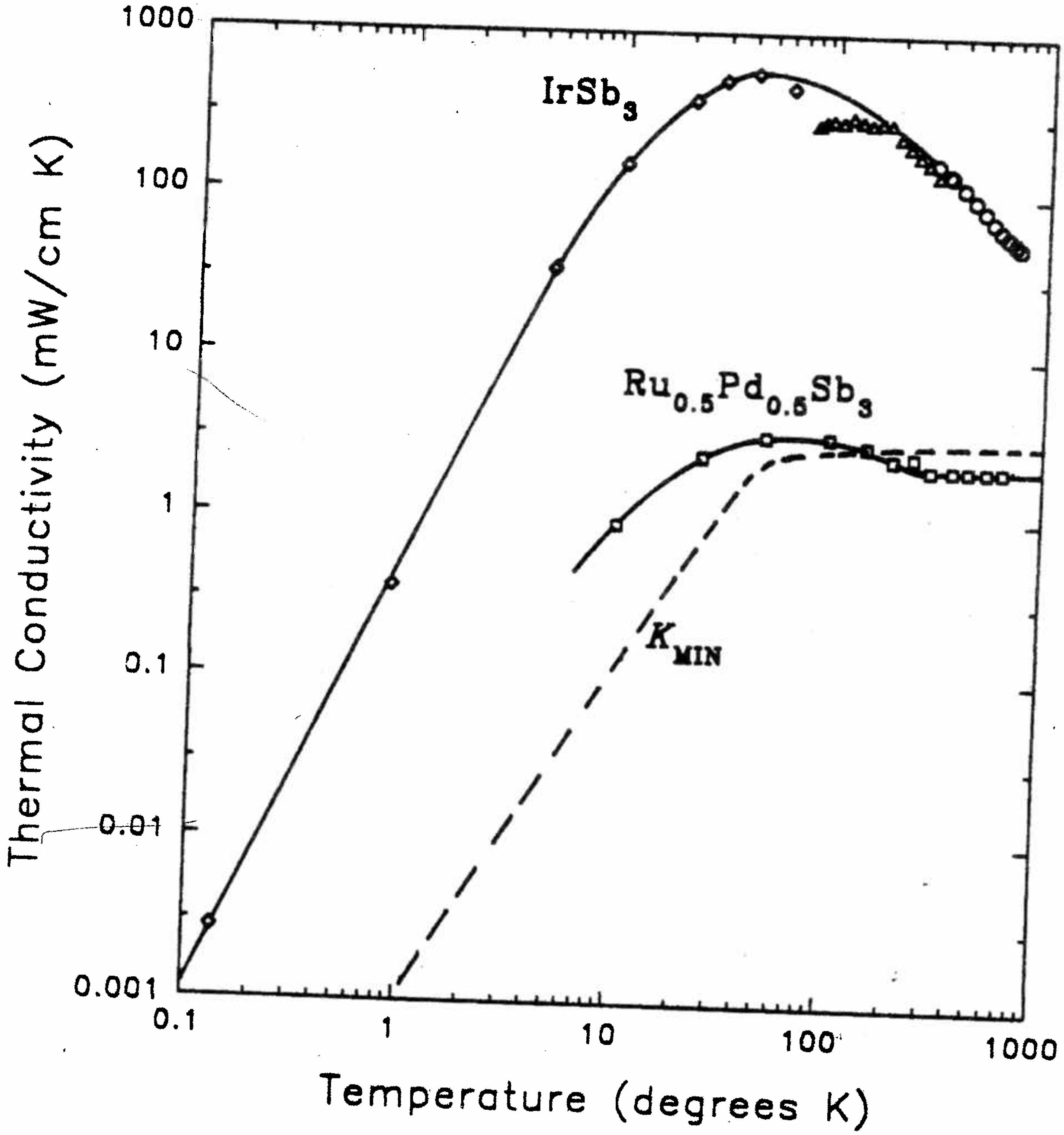
**NEW: HOLEY**

**OLD: UNHOLEY**

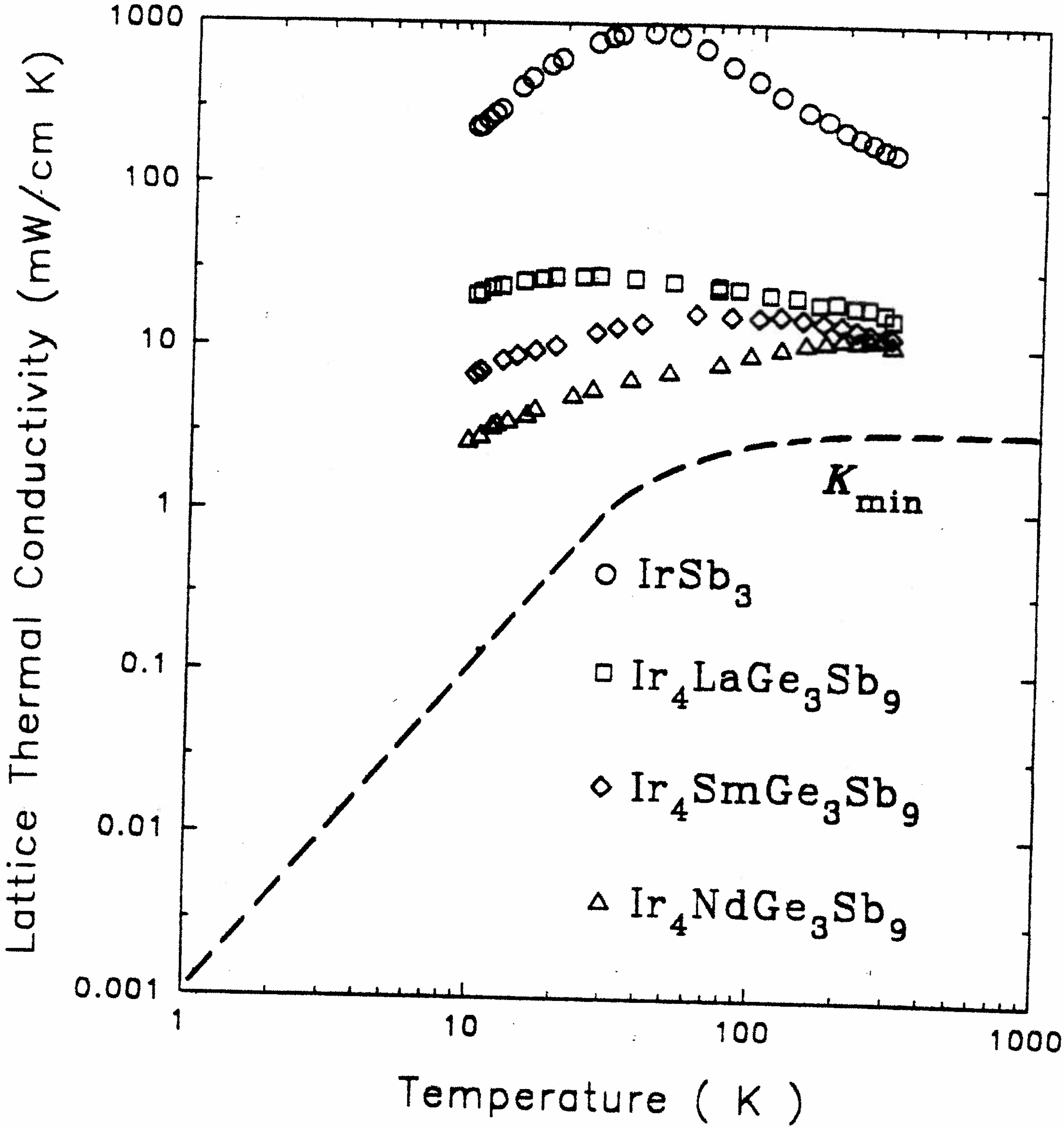



Skutterudit-Struktur.

# Thermal Conductivity of $IrSb_3$




G.S. Nolas, V.G. Harris, T.M. Tritt, and G.A. Slack, J. of Appl. Phys. 80, 6304- 6308 (1996, July)




G.S. Nolas, G.A. Slack, T.M. Tritt, and D.T. Morelli, Fourteenth International Conference on Thermoelectrics, St. Petersburg, (June, 1995) p. 236-239

N36

# SERENDIPITY IN SCIENCE

1. ROSS AND ANDERSON, UMEÅ, SWEDEN, 1980

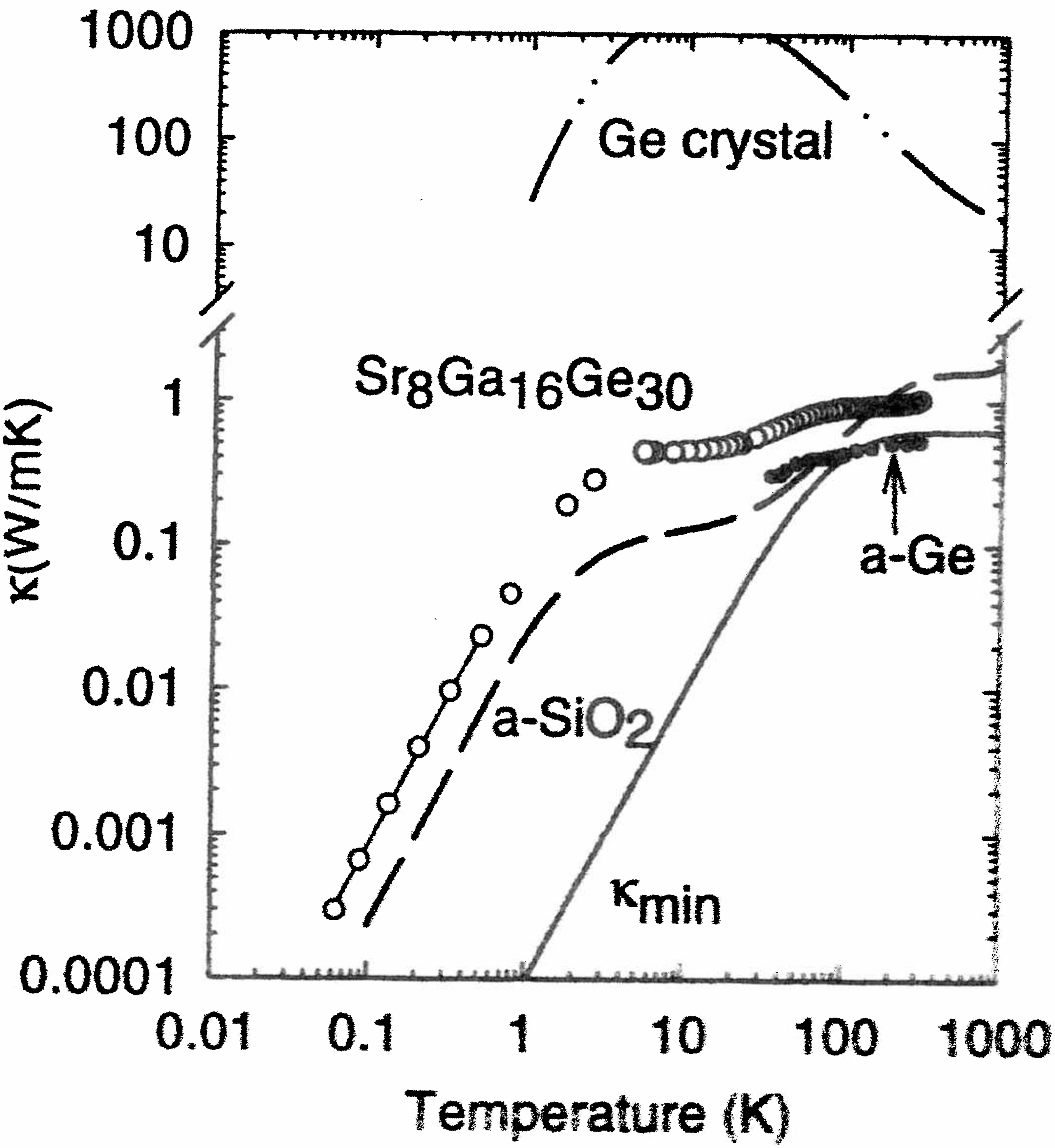
2. DOWNTOWN UMEÅ HAS GIANT "ICE" STALAGMITE

3. R.&A., 1982, $K_g$ OF T.H.F. IN ICE

4. CROS, 1965, BORDEAUX, FRANCE, MADE Si AND GE CLATHRATES

5. CROS, 1989. WORKED IN BORDEAUX IN HIS LAB, LEARNED ABOUT Si & Ge

6. ?? DO Si & Ge CLATHRATES HAVE LOW $K_g$




## Glass-Like Heat Conduction in Crystalline Semiconductors


G. S. NOLAS, J. L. COHN, B. C. CHAKOUMAKOS and G. A. SLACK



THERMAL CONDUCTIVITY 25–THERMAL EXPANSION 13-
JUNE 13–16, 1999 p.122

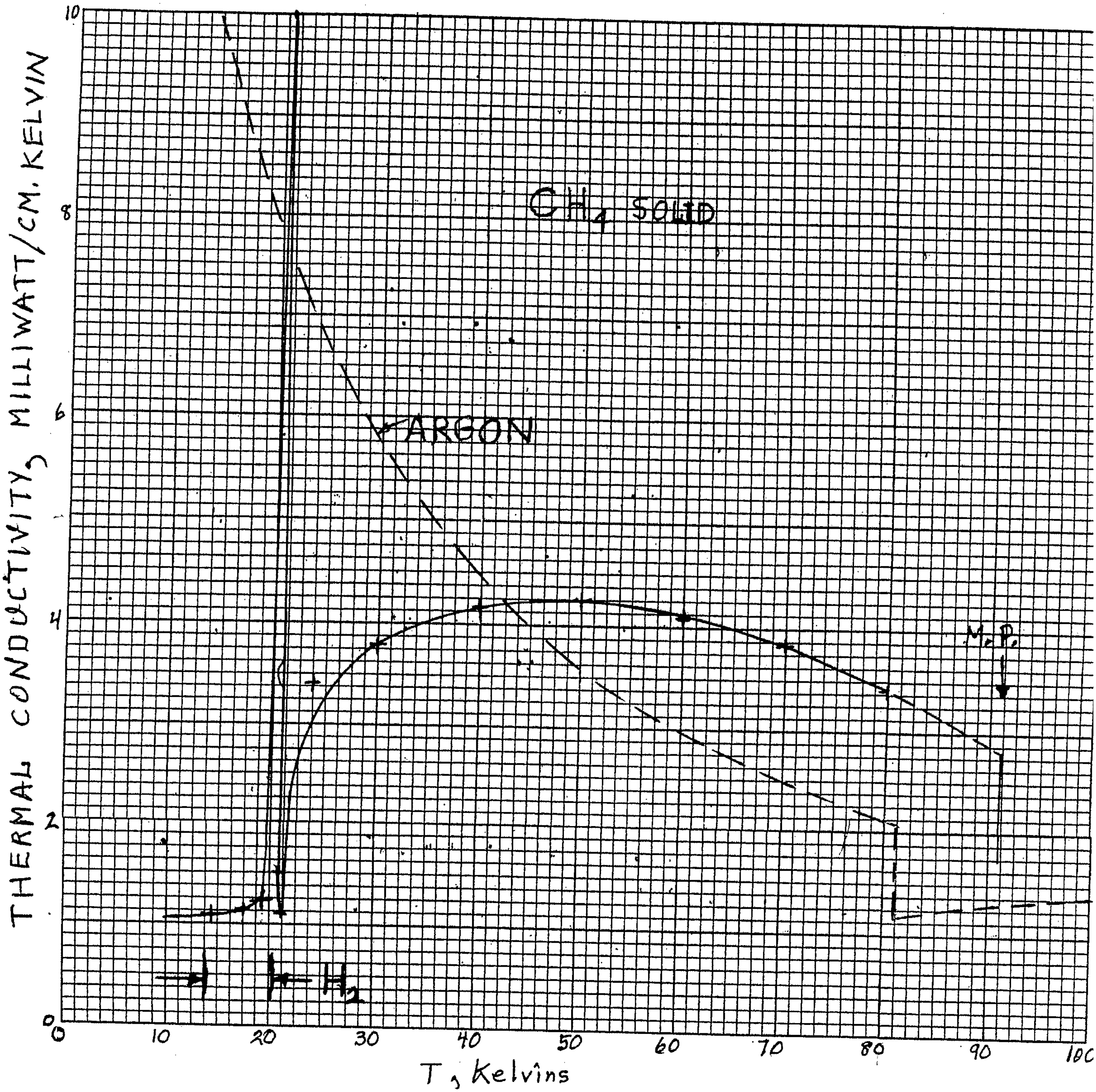
# Why Clathrates are Good Thermoelectrics: A Theoretical Study of $Sr_8Ga_{16}Ge_{30}$

Nick P. Blake, Lone Møllnitz, Georg Kresse, & Horia Metiu

JOURNAL OF CHEMICAL PHYSICS 111, 3133-3144 (1999)

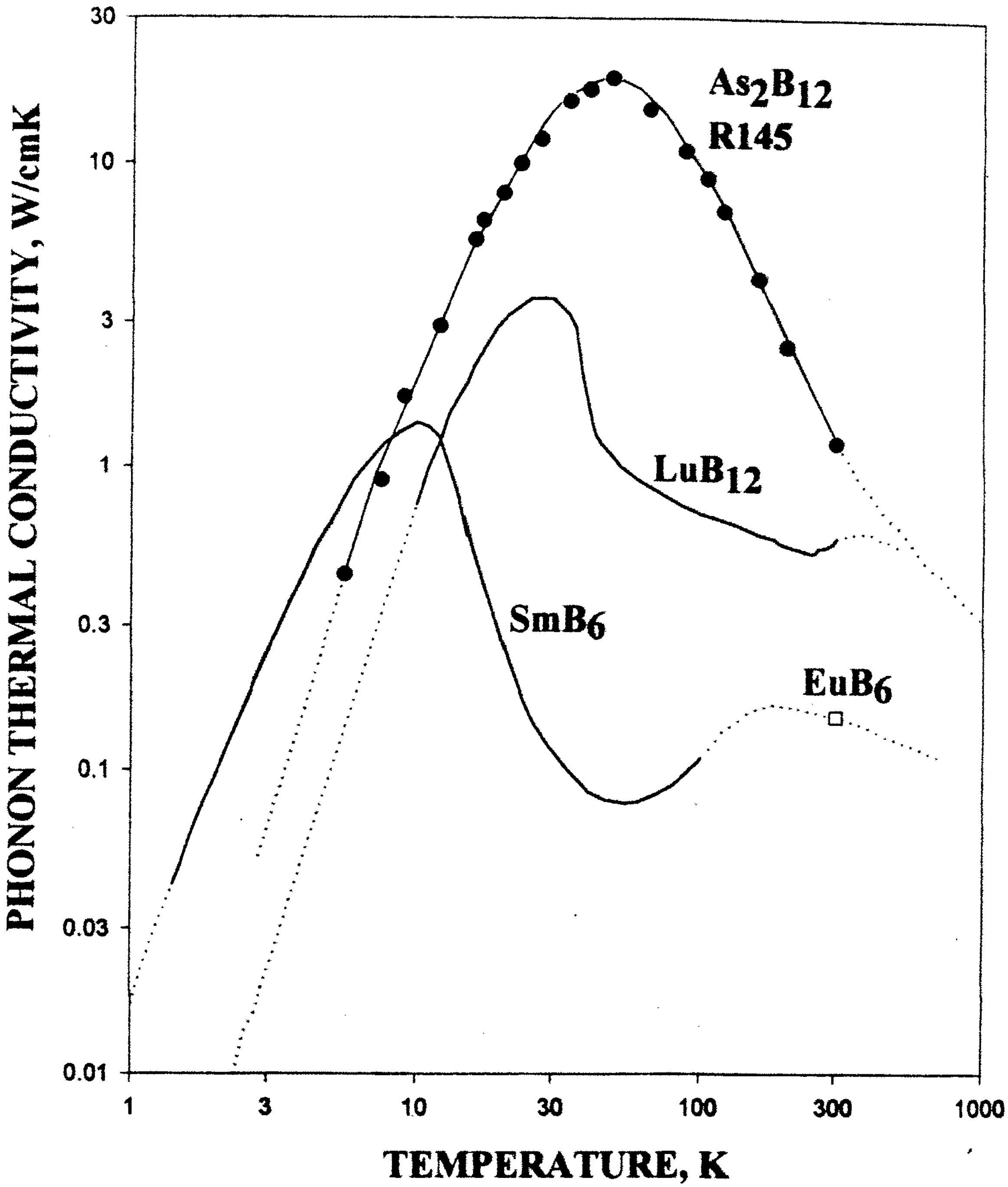
This clathrate is a PGEC (phonon glass-electron crystal) material in which the rattling (Sr) atoms scatter phonons but do not disturb the conduction electrons. "...to a first approximation (the) Sr atoms are neutral. There is little charge transfer between Sr atoms and the frame."

"...the (PGEC) proposal works surprisingly well."




Below 22 Kelvin: A.N. Gerritsen and P. Vanderstar, Physica 9, 503 (1942)

Above 22 Kelvin: V.G. Manzhelii and I.N. Krupski, Soviet Physics – Solid State 10, 221 (1968)




HIGH THERMAL CONDUCTIVITY
AND
LOW THERMAL CONDUCTIVITY
SOLIDS

GLEN A. SLACK

THERMAL CONDUCTIVITY 25–THERMAL EXPANSION 13-
JUNE 13–16, 1999 p.308

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