A MODEL FOR THE THERMOELECTRIC PROPERTIES OF N-TYPE SILICON-GERMANIUM ALLOYS

PRESENTED BY

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SILICON-GERMANIUM INTEGRATION MEETING
WALTHAM, MA

THERMOELECTRIC PROPERTIES MODEL

LONG TERM GOAL: DEVELOP A PREDICTIVE, QUANTITATIVE, THEORETICALLY JUSTIFIABLE AND SELF-CONSISTENT MODEL OF ALL OF THE THERMOELECTRIC PROPERTIES OF SILICON-GERMANIUM ALLOYS.

STATUS:

- o COMPLETE MODEL DEVELOPED FOR N-TYPE SiGe
- o DETAILED DOCUMENTATION FOR GENERAL DISTRIBUTION EXPECTED BY END OF 89
- o MUCH HIGHER ZT, MODIFIED SILICON-GERMANIUM MODELS UNDER DEVELOPMENT
- o MODEL FOR P-TYPE SiGe UNDER DEVELOPMENT

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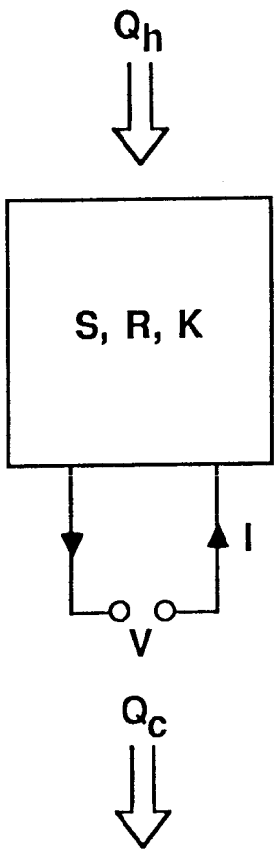
BASIC THERMOELECTRICITY



Heat Source

Thermoelectrics

Load

Heat Sink

Conversion Efficiency

$$\eta = \frac{IV}{Q_h}$$

$$= \frac{I\,(S\Delta T - IR)}{IST_h + K\Delta T - 1/2\, I^2 R}$$

Optimize Current

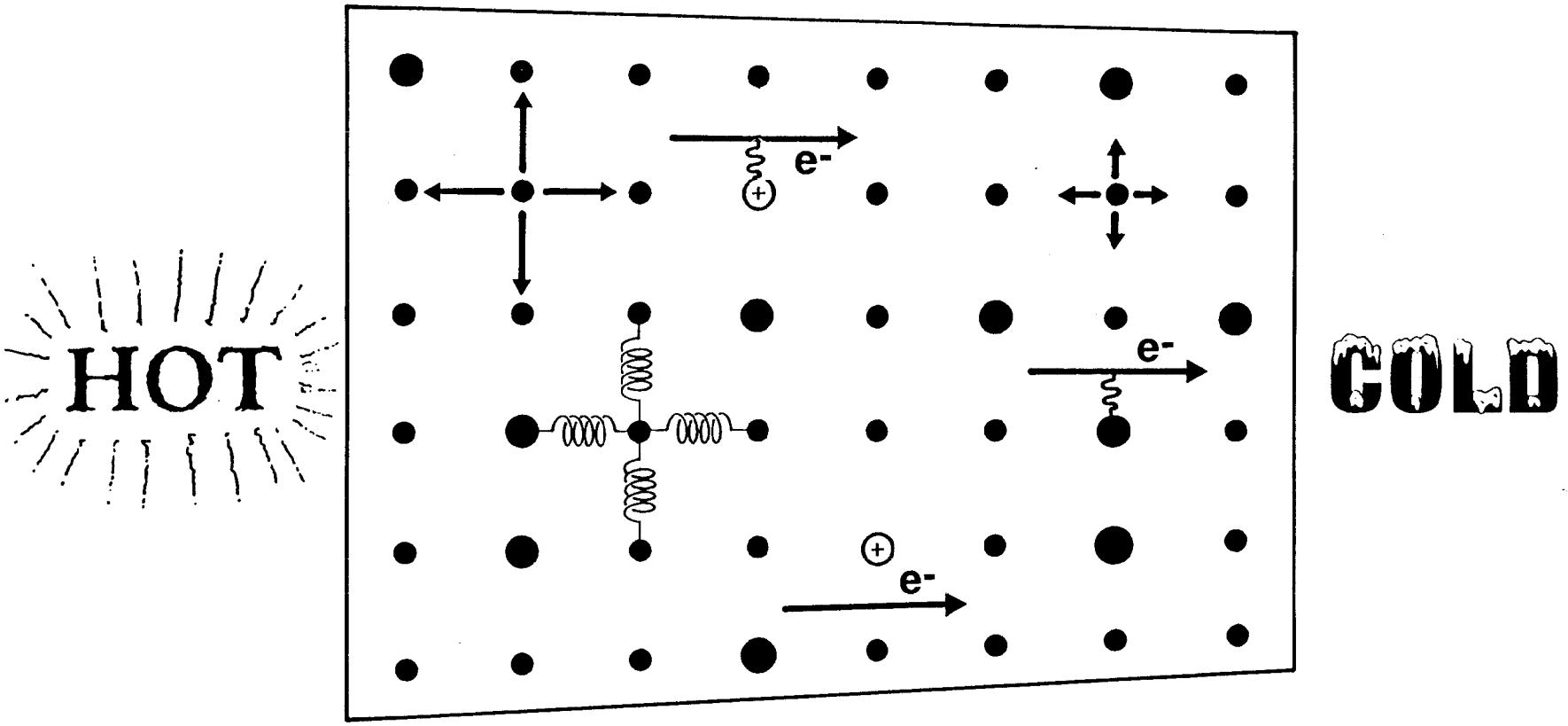
$$\eta_{opt} = \frac{\Delta T}{T_h}\ \frac{\sqrt{1 + Z\bar{T}} - 1}{\sqrt{1 + Z\bar{T}} + T_c/T_h}$$

Where

$$Z\bar{T} \equiv \frac{S^2 T_{average}}{R\,K}$$

JPL

THERMOELECTRIC MATERIAL MODEL



HEAT IN + THERMOELECTRIC ELEMENT ⇒ ELECTRICAL POWER

THERMOELECTRIC PROPERTIES MODEL

BASIC APPROACH:

- Keep the model as simple as possible.
- Use standard transport integrals
  - Boltmann's equation in the relaxation time approximation
  - Electrical calculations after Fistul
  - Lattice k calculations after Steigmeier and Abeles, 1964
- Include effects of Fermi Statistics
- Account for minority carrier effects
  - For simplicity, use same parameters for holes and electrons

THERMOELECTRIC PROPERTIES MODEL

SCATTERING MECHANISMS:

- Two scattering mechanisms for charge carriers
  - Acoustic lattice vibrations
  - Ionized impurities
- Three scattering mechanisms for phonons
  - Phonon-phonon scattering (both Normal and Umklapp)
  - Point defect scattering (mass and strain fluctuations)
  - Charge carriers
- Details in the Appendix

THERMOELECTRIC PROPERTIES MODEL

LEAST SQUARES FIT PROCEDURE

- o Experimental database
  - R, Q and K from 4 RCA-Princeton zone leveled samples (Dismukes et al, 1964)
  - R, Q and K from 2 RCA-Harrison zone leveled samples (RCA Topical Report, 1969)
  - R, mobility, Q and K on silicon (various literature sources, mostly)
  - R and Q from T373 and T106 (Thermo Electron)
  - R and high temperature mobility from T373 and silicon (JPL)

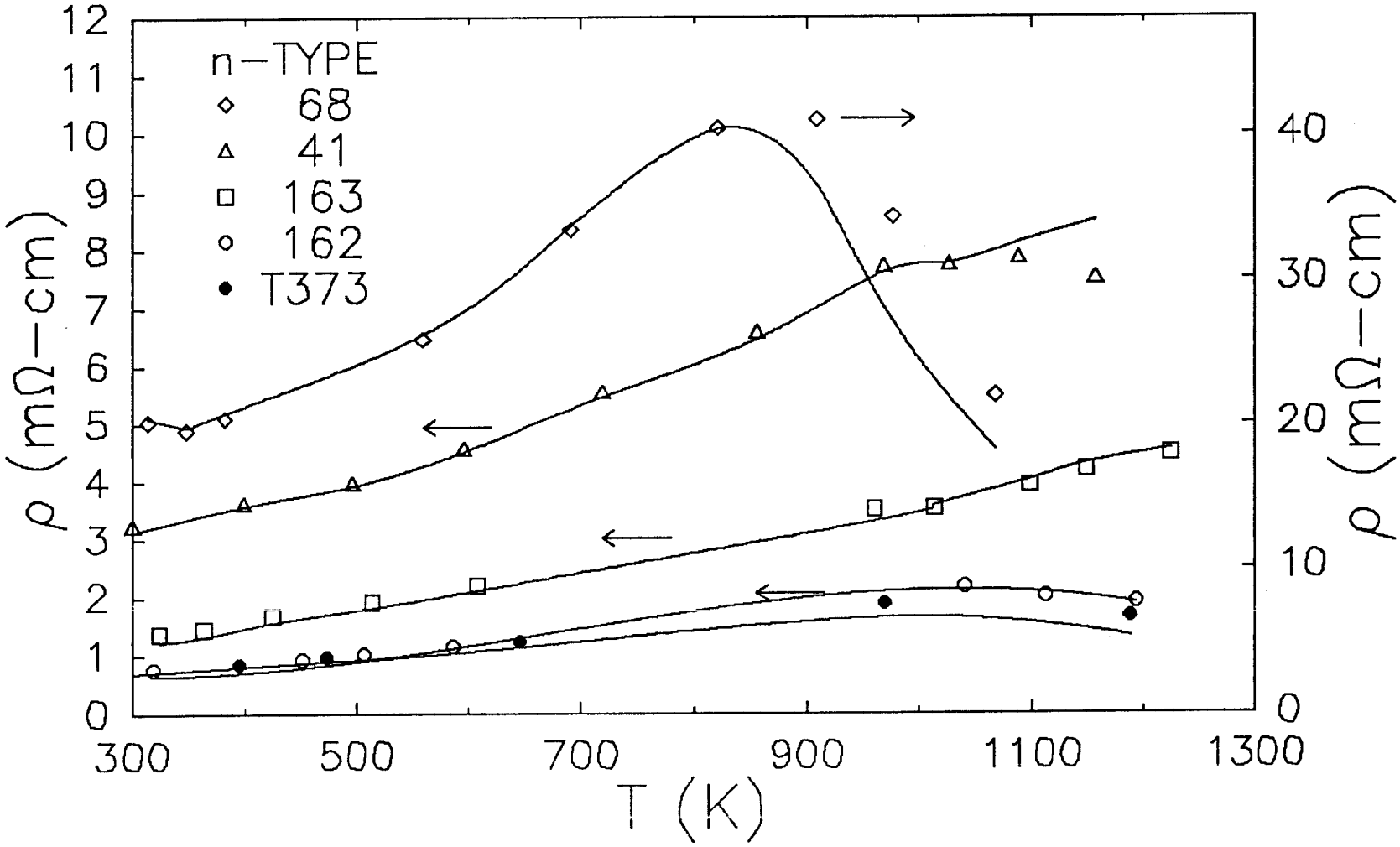
- o Calculate R, Q, mobility and K for each data point
  - Silicon/germanium content and temperature are known
  - Use a guess for the adjustable parameters: effective mass, deformation potential and dielectric constant
  - Optimize chemical potential (ie doping level) for each data point

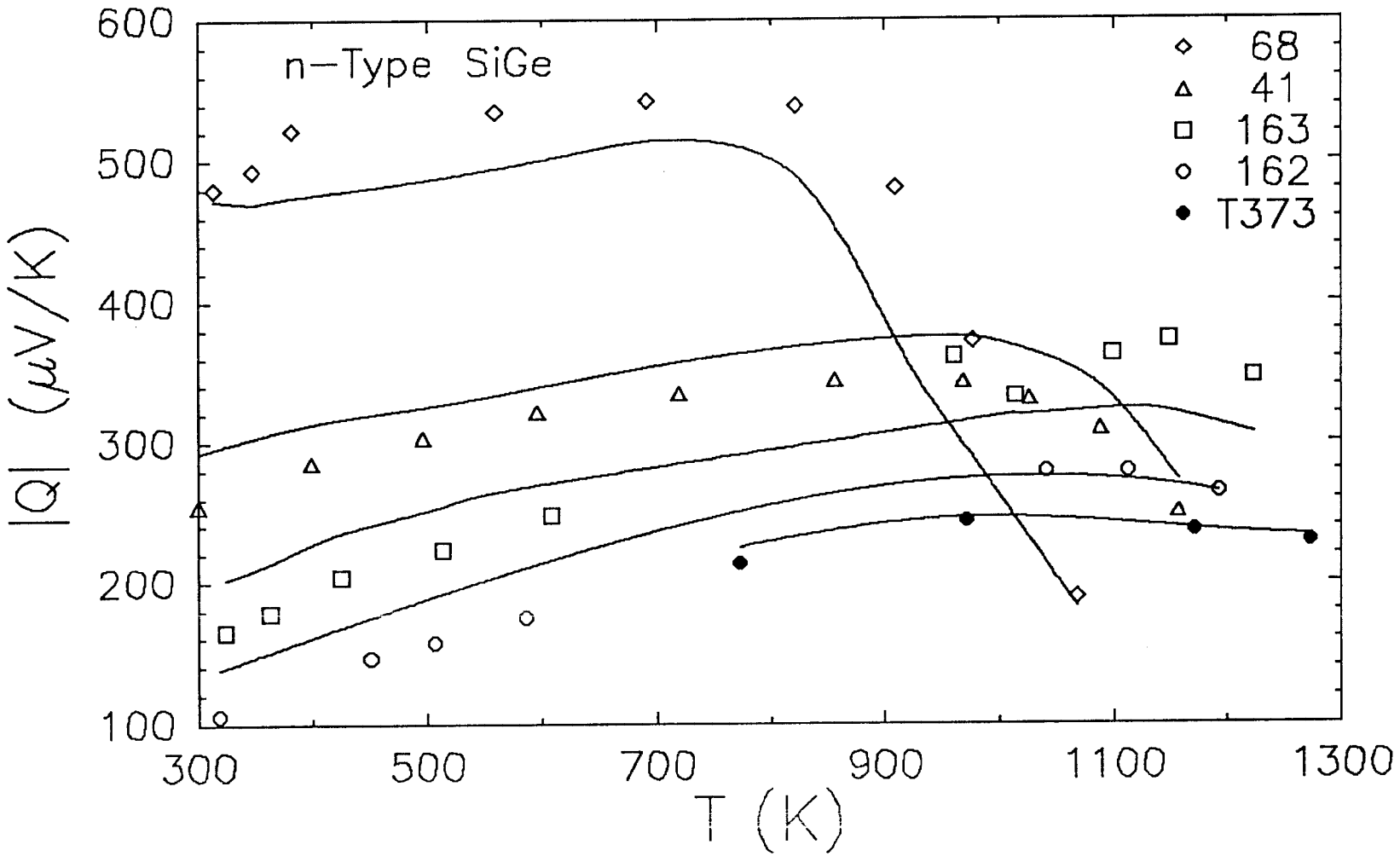
- o Optimize parameters (re-adjusting chemical potential each time)

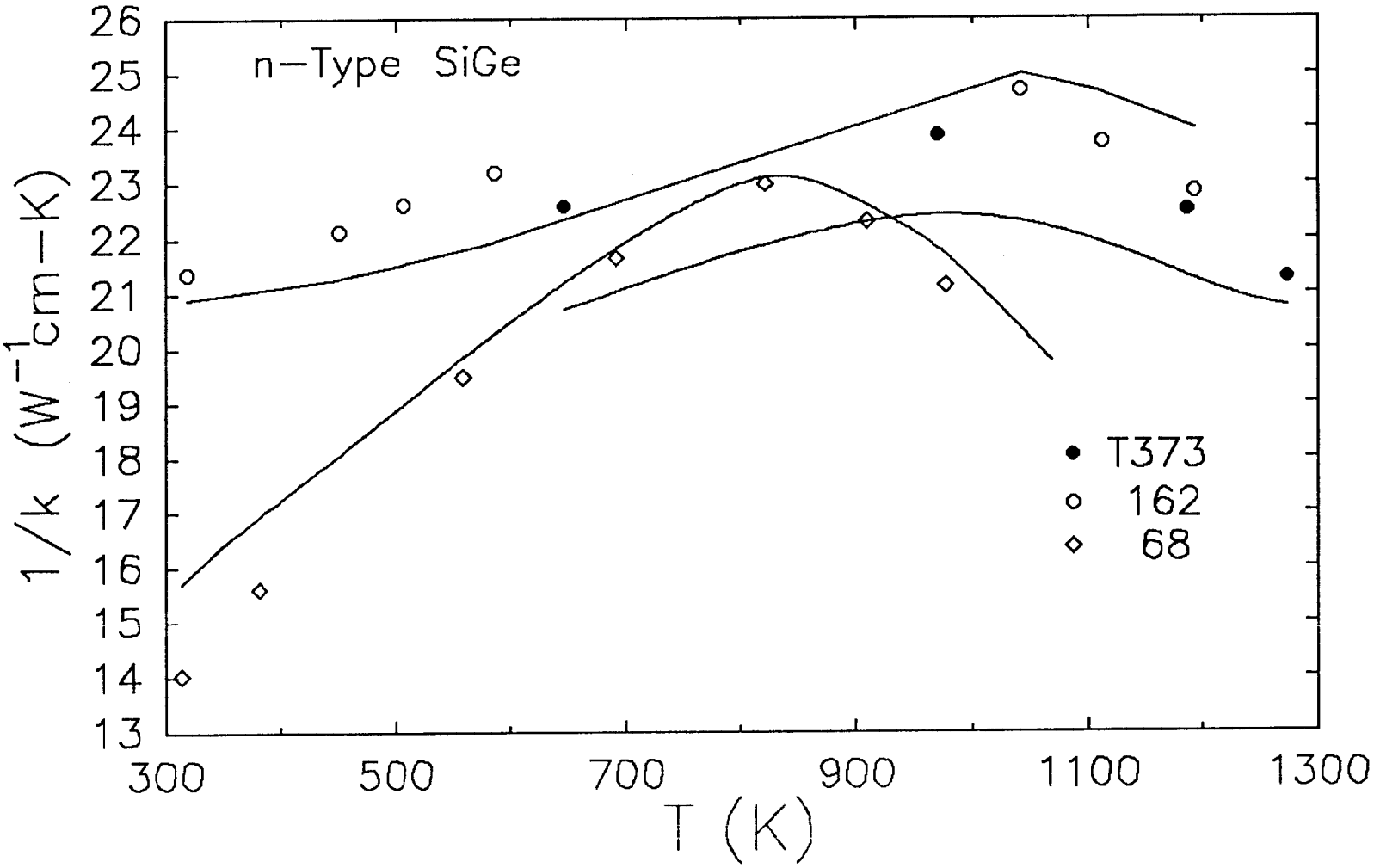
THERMOELECTRIC PROPERTIES MODEL

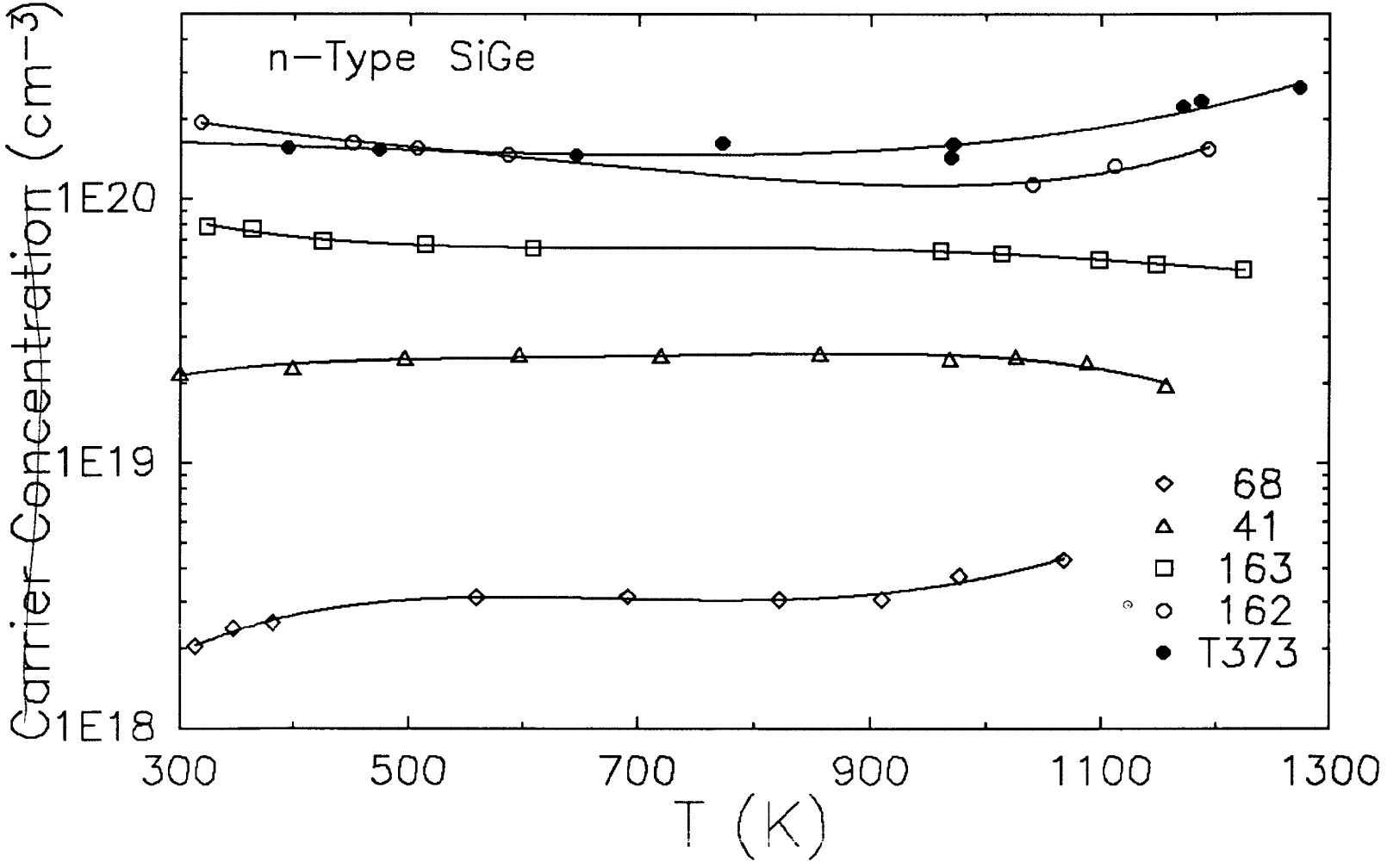
RESULTS

- o COMPARISON WITH EXPERIMENTAL DATA


n–TYPE
68
41
163
162
T373
ρ (mΩ–cm)
ρ (mΩ–cm)
T (K)
0
1
2
3
4
5
6
7
8
9
10
11
12
0
10
20
30
40
300
500
700
900
1100
1300


n–Type SiGe
68
41
163
162
T373
600
500
400
300
200
100
|Q| (μV/K)
300
500
700
900
1100
1300
T (K)


n–Type SiGe
1/k (W^{-1}cm–K)
T (K)
26
25
24
23
22
21
20
19
18
17
16
15
14
13
300
500
700
900
1100
1300
T373
162
68



Ionized Dopant Density

E2

THERMOELECTRIC PROPERTIES MODEL

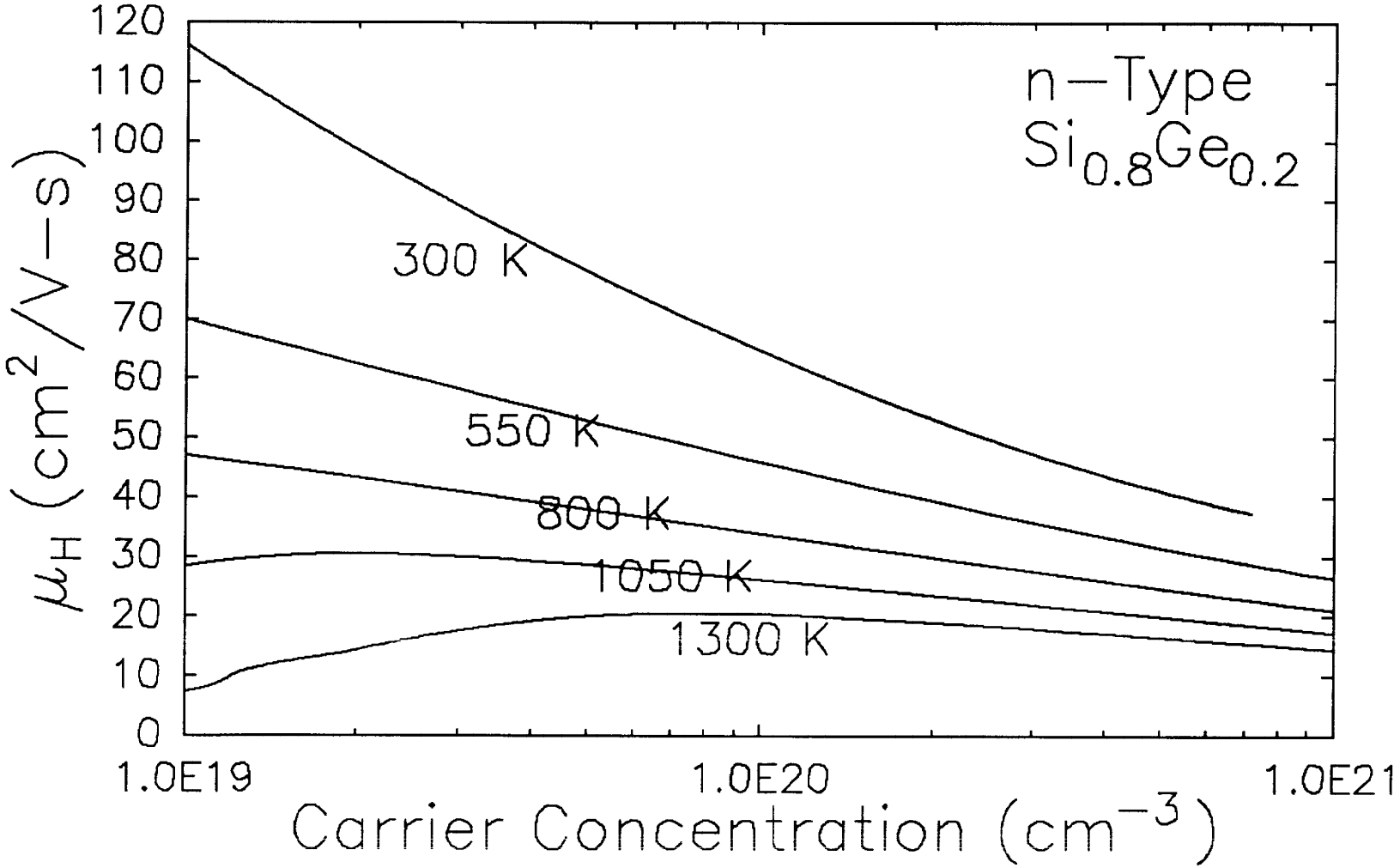
RESULTS

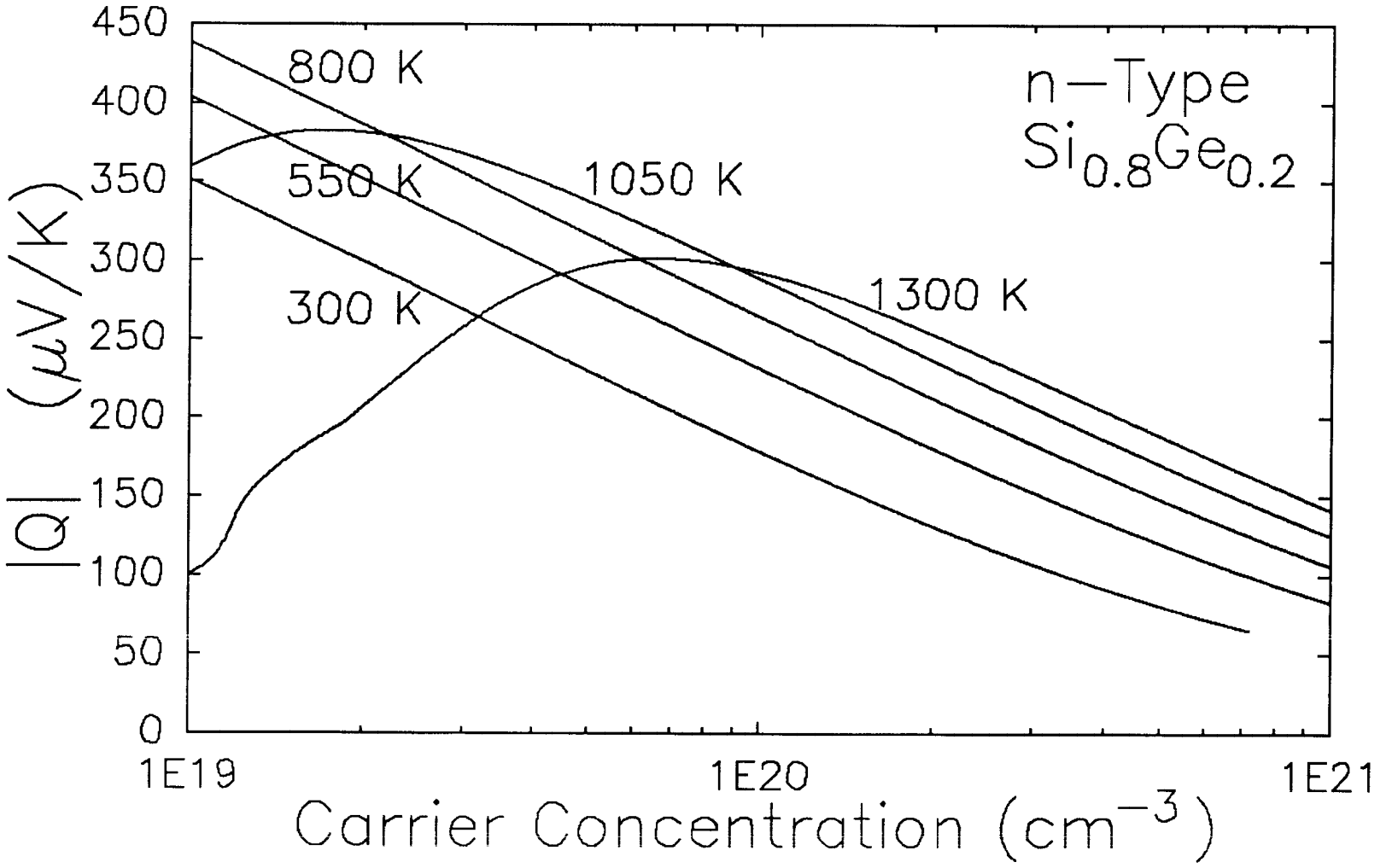
- o THE CALCULATED DOPING LEVELS ARE REASONABLE
  - JUSTIFIES TREATING CHEMICAL POTENTIAL AS AN ADJUSTABLE PARAMETER
- o REPRODUCES ALL QUALITATIVE TRENDS WELL
  - TEMPERATURE, DOPING AND SI/GE DEPENDENCIES ARE RELIABLY REPRODUCED
- o THERMAL CONDUCTIVITY IS WELL DESCRIBED
  - TWO PARAMETERS FROM THE LITERATURE NEEDED TO DESCRIBE UNDOPED SI
  - NO FURTHER ADJUSTABLE PARAMETERS ARE REQUIRED, BEYOND THOSE NEEDED FOR FITTING THE ELECTRICAL PROPERTIES ALONE
- o GREATEST ERRORS ARE:
  - OVER-ESTIMATION OF SEEBECK AT LOWER TEMPERATURES
  - OVER-ESTIMATION OF MOBILITY AT HIGHER TEMPERATURES

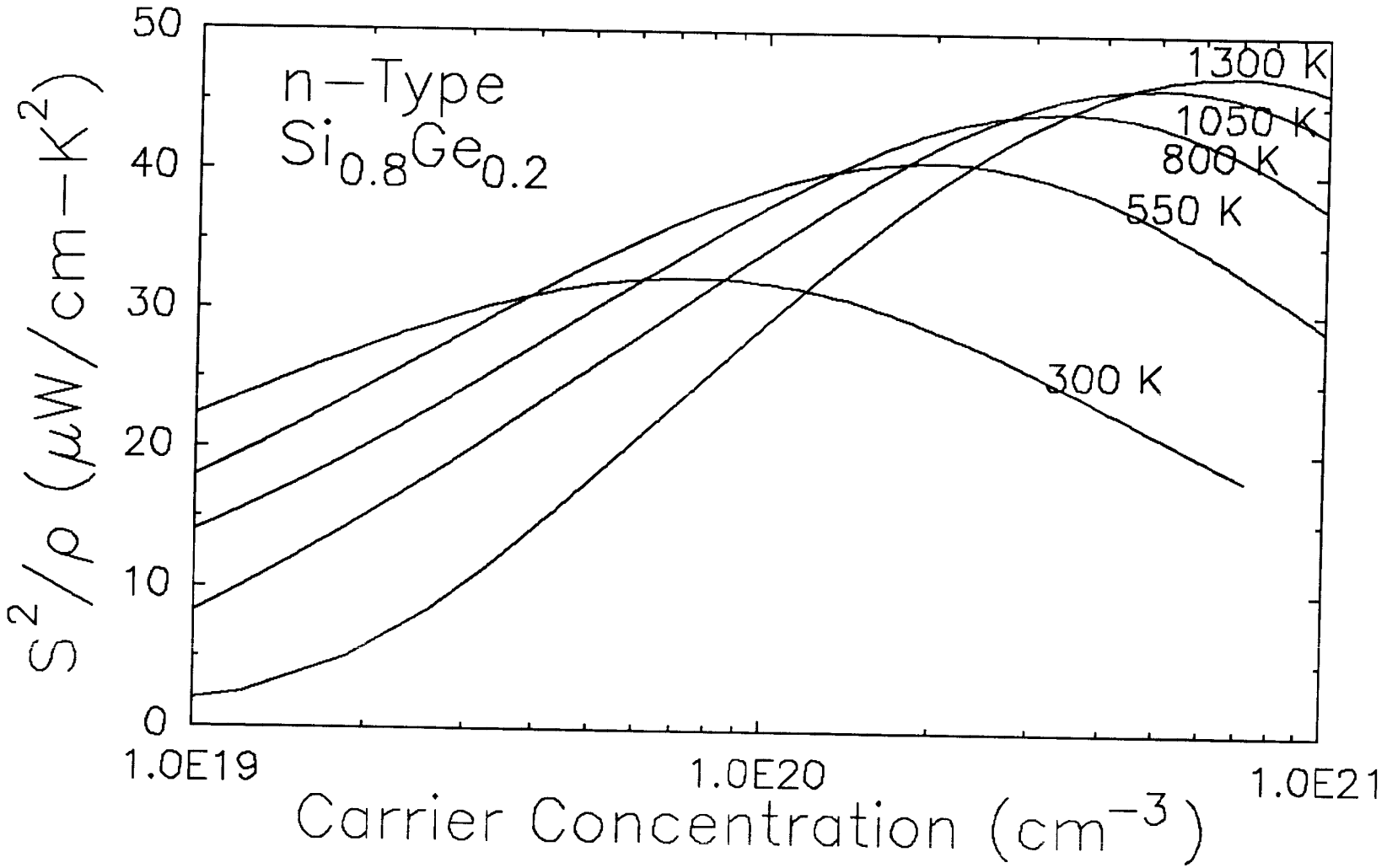
THERMOELECTRIC PROPERTIES MODEL

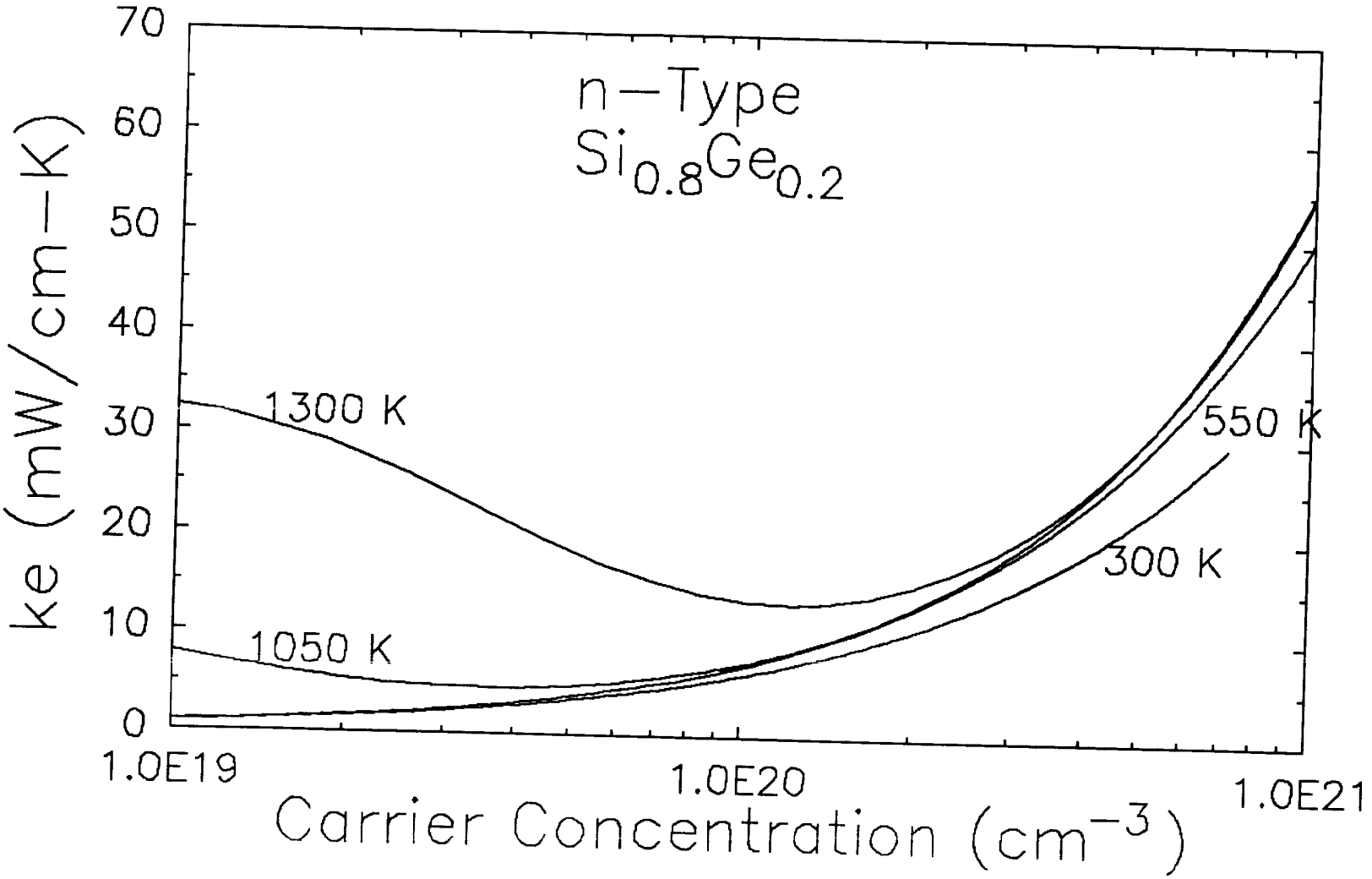
RESULTS

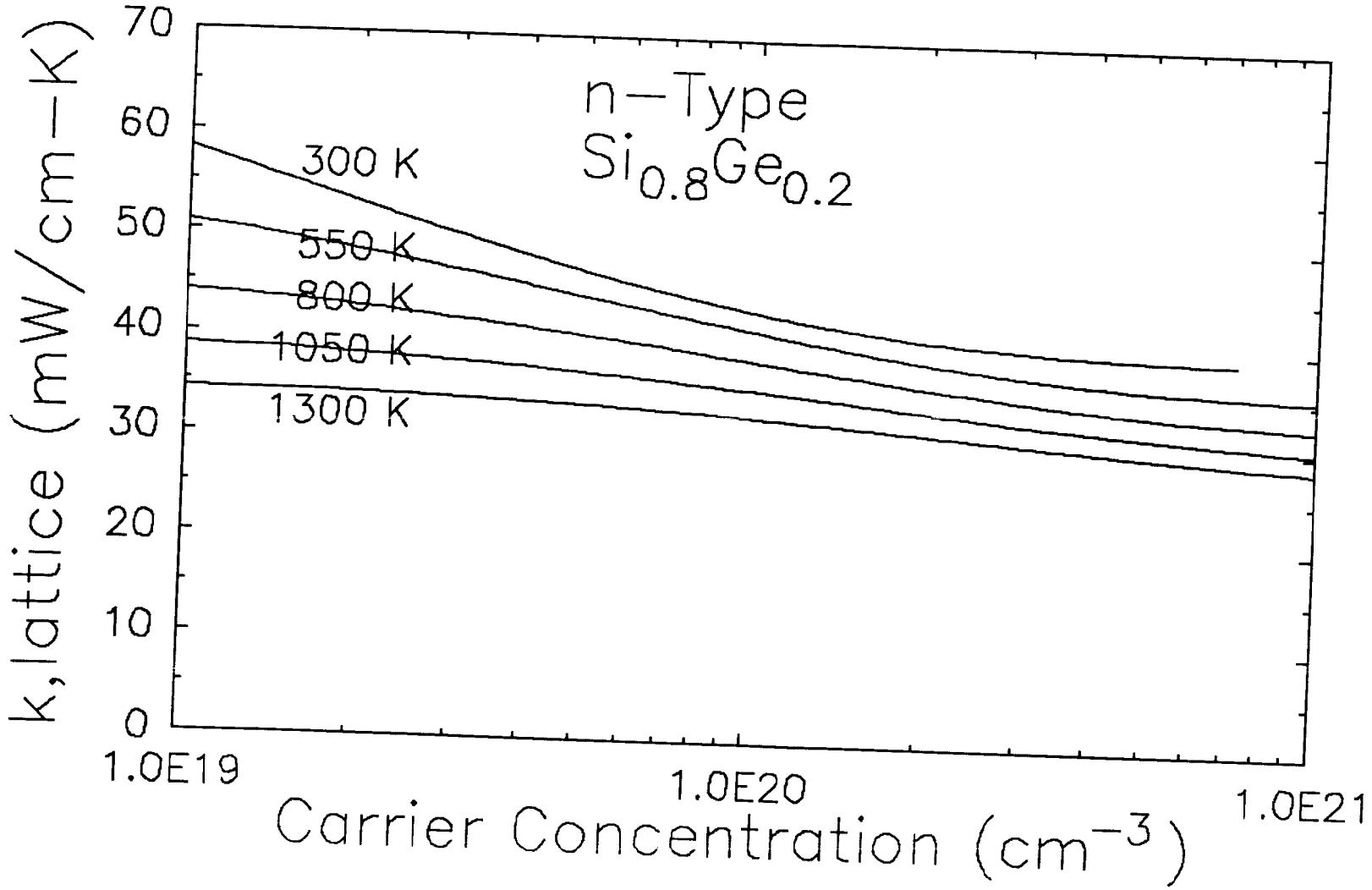
- o DOPING DEPENDENCIES

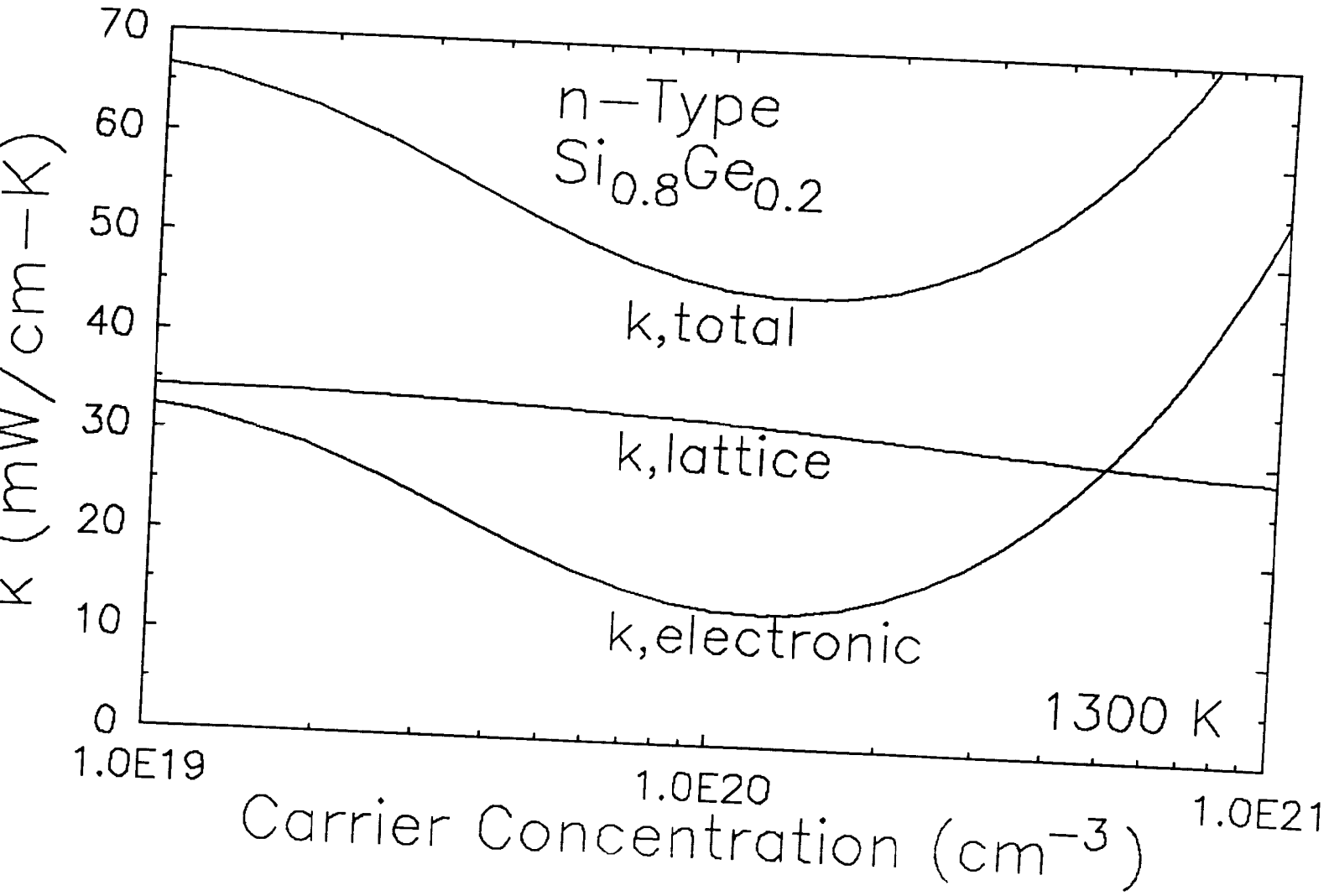

n–Type
$Si_{0.8}Ge_{0.2}$
300 K
550 K
800 K
1050 K
1300 K
120
110
100
90
80
70
60
50
40
30
20
10
0
μ_H (cm^2/V–s)
1.0E19
1.0E20
1.0E21
Carrier Concentration (cm^{-3})

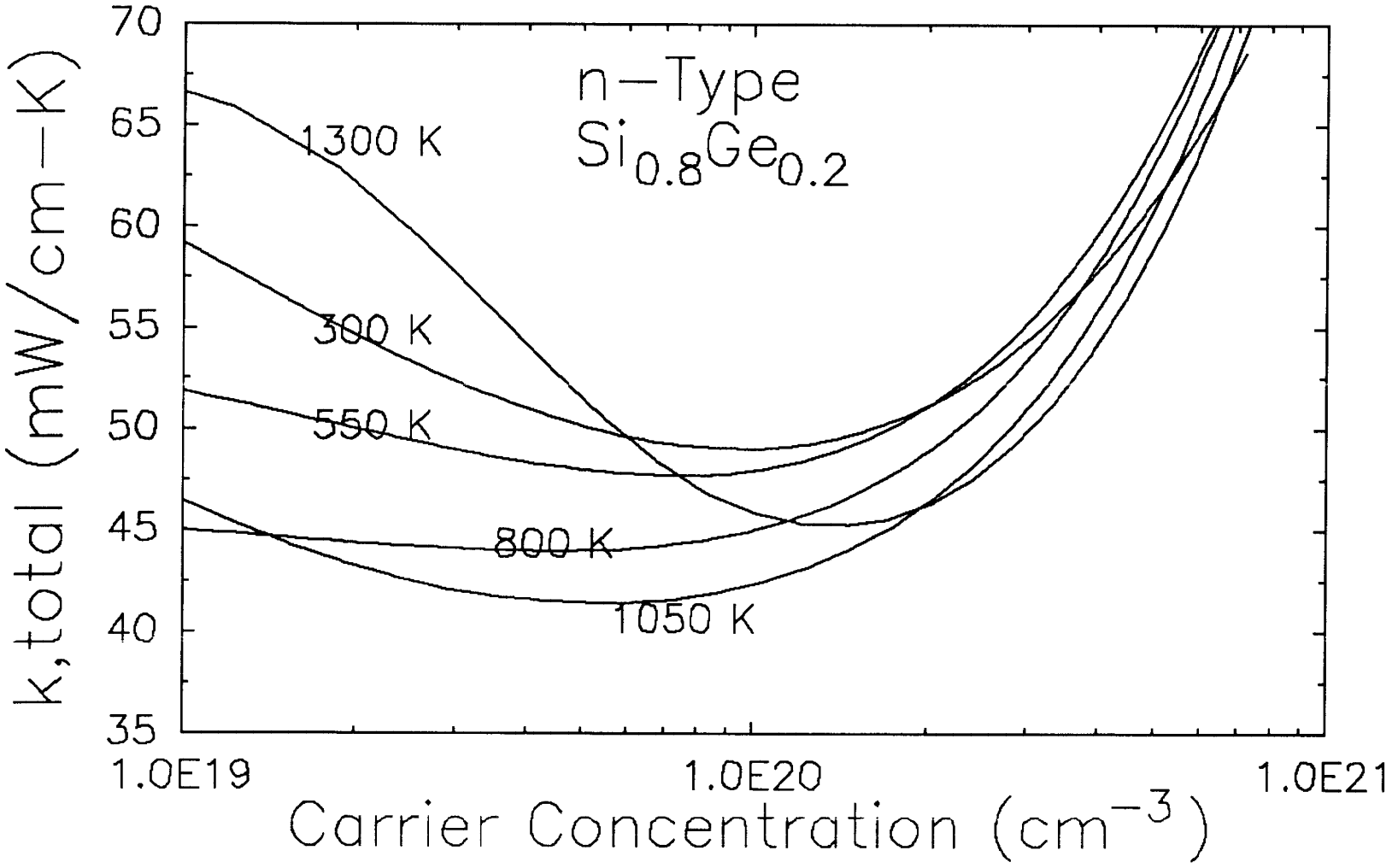

450
400
350
300
250
200
150
100
50
0
|Q| (μV/K)
800 K
550 K
300 K
1050 K
1300 K
n–Type
Si0.8Ge0.2
1E19
1E20
1E21
Carrier Concentration (cm−3)

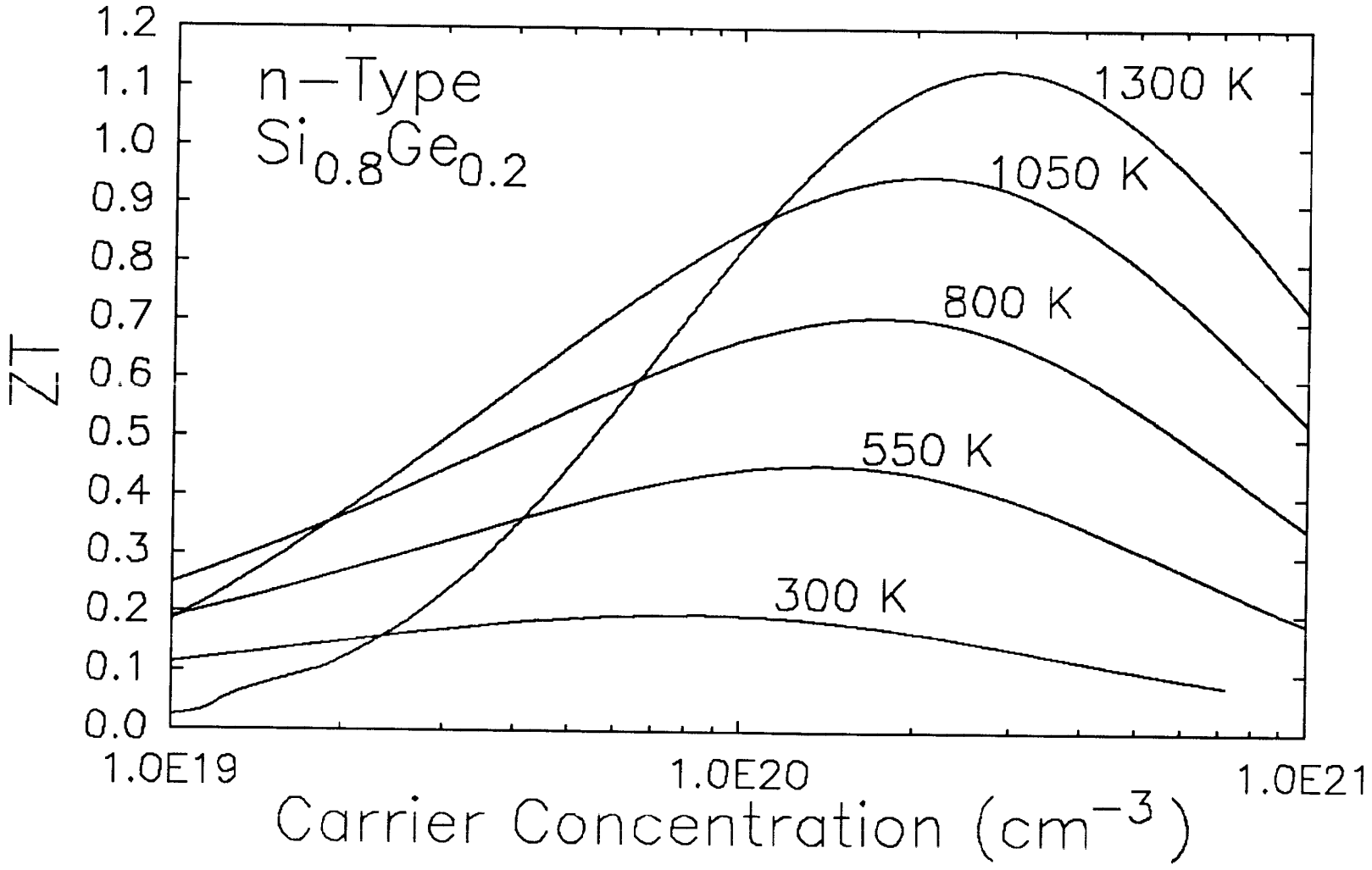

n–Type
$Si_{0.8}Ge_{0.2}$
1300 K
1050 K
800 K
550 K
300 K
50
40
30
20
10
0
1.0E19
1.0E20
1.0E21
S^2/ρ ($\mu W/cm-K^2$)
Carrier Concentration (cm^{-3})


n–Type
$Si_{0.8}Ge_{0.2}$
ke (mW/cm–K)
70
60
50
40
30
20
10
0
1300 K
1050 K
550 K
300 K
1.0E19
1.0E20
1.0E21
Carrier Concentration (cm^{-3})

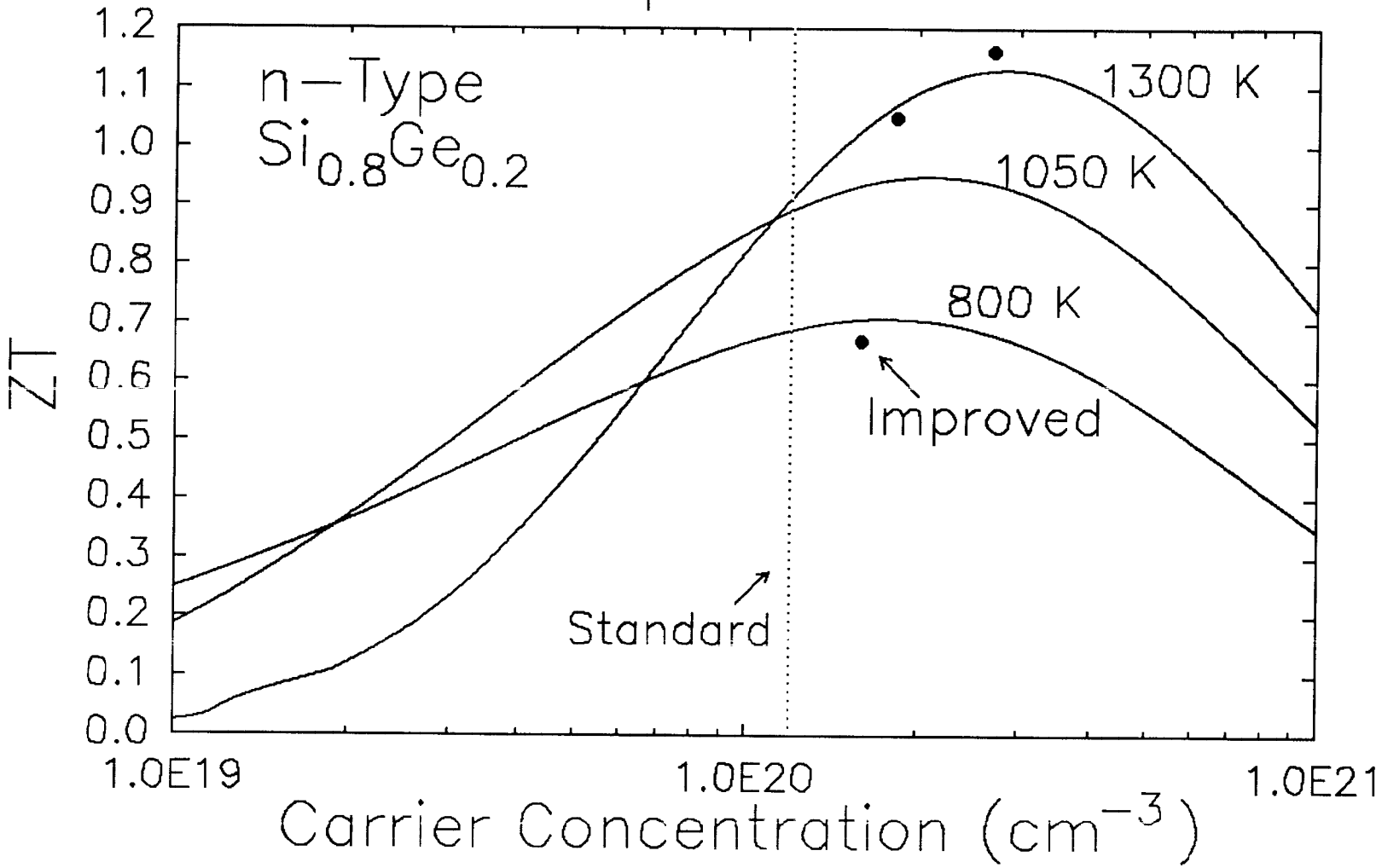

n–Type
$Si_{0.8}Ge_{0.2}$
300 K
550 K
800 K
1050 K
1300 K
k, lattice (mW/cm–K)
70
60
50
40
30
20
10
0
1.0E19
1.0E20
1.0E21
Carrier Concentration (cm^{-3})


n–Type
$Si_{0.8}Ge_{0.2}$
k,total
k,lattice
k,electronic
1300 K
70
60
50
40
30
20
10
0
k (mW/cm–K)
1.0E19
1.0E20
1.0E21
Carrier Concentration (cm^{-3})


n–Type
$Si_{0.8}Ge_{0.2}$
1300 K
300 K
550 K
800 K
1050 K
k,total (mW/cm–K)
70
65
60
55
50
45
40
35
1.0E19
1.0E20
1.0E21
Carrier Concentration (cm^{-3})


n–Type
$Si_{0.8}Ge_{0.2}$
1300 K
1050 K
800 K
550 K
300 K
ZT
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1.0E19
1.0E20
1.0E21
Carrier Concentration (cm^{-3})

Electrical and Thermal Model For Improved SiGe

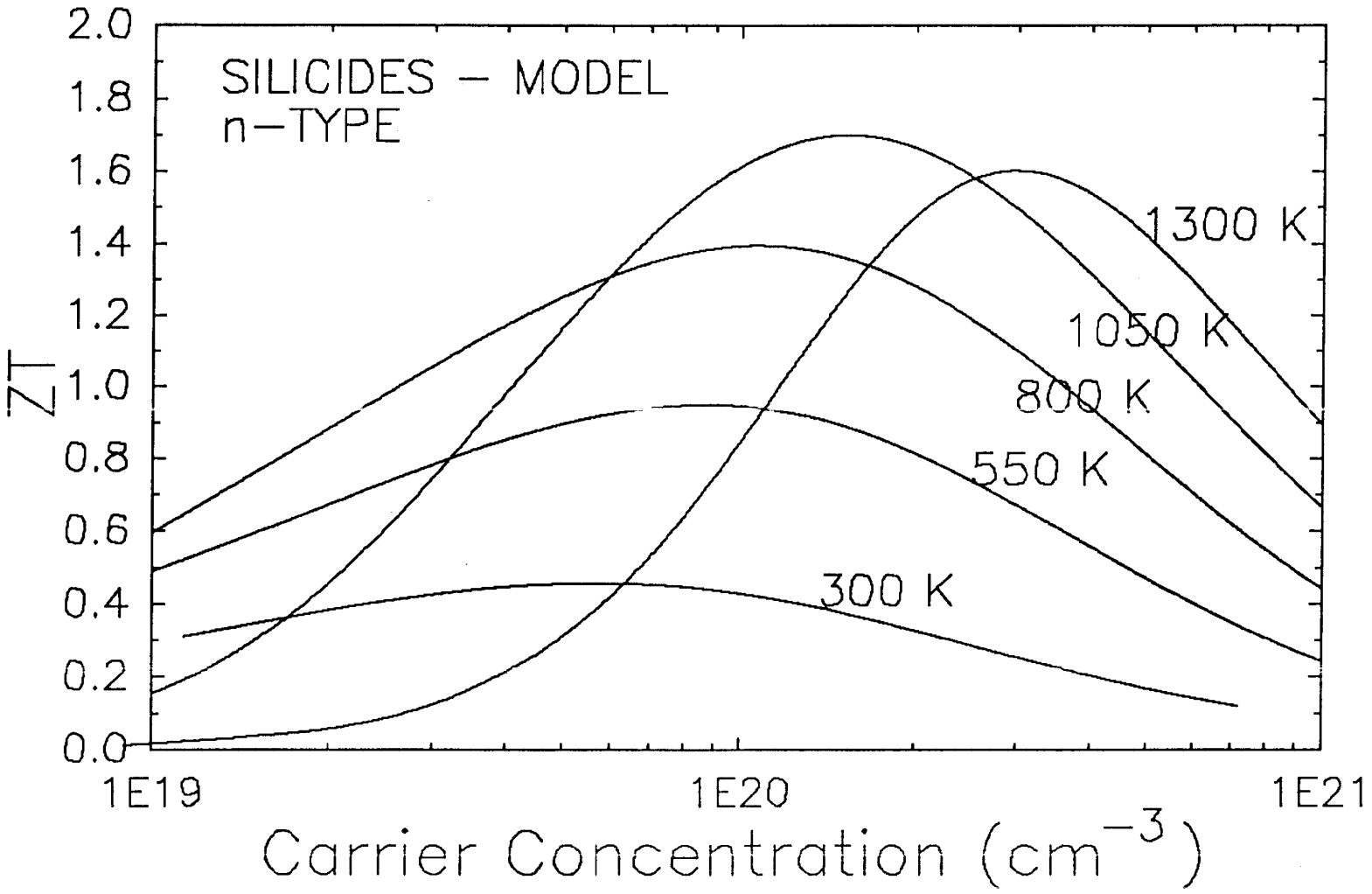


THERMOELECTRIC PROPERTIES MODEL

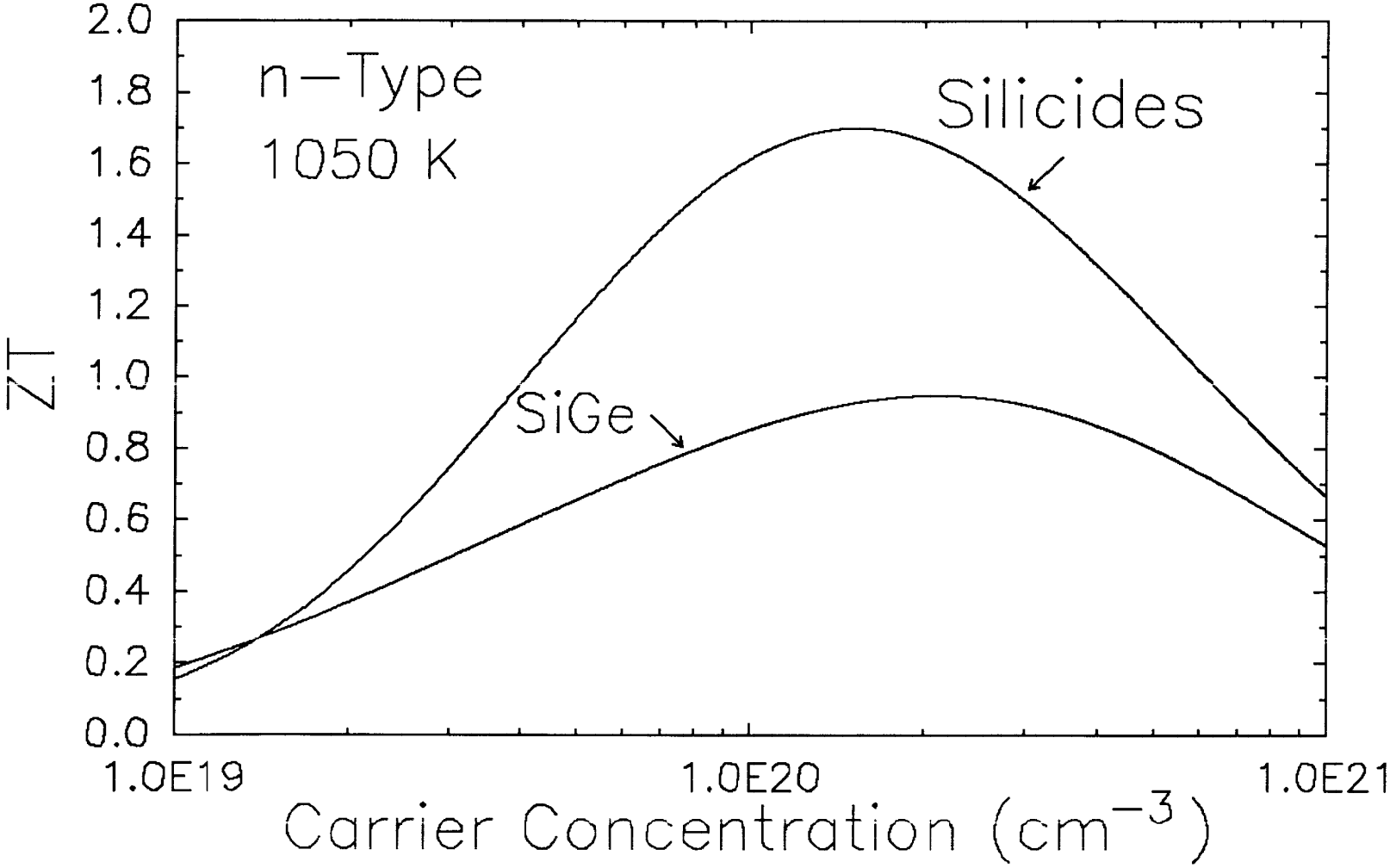
FUTURE EFFORTS:

- o Apply model to p-type SiGe
- o Examine the importance of phonon drag effects (neglected here)
- o Examine methods to enhance the figure of merit
  - Grain boundary scattering of phonons
  - Resonance scattering of phonons by inclusions
  - Increased mass difference (ie Si-Pb solid solutions)
  - etcetera

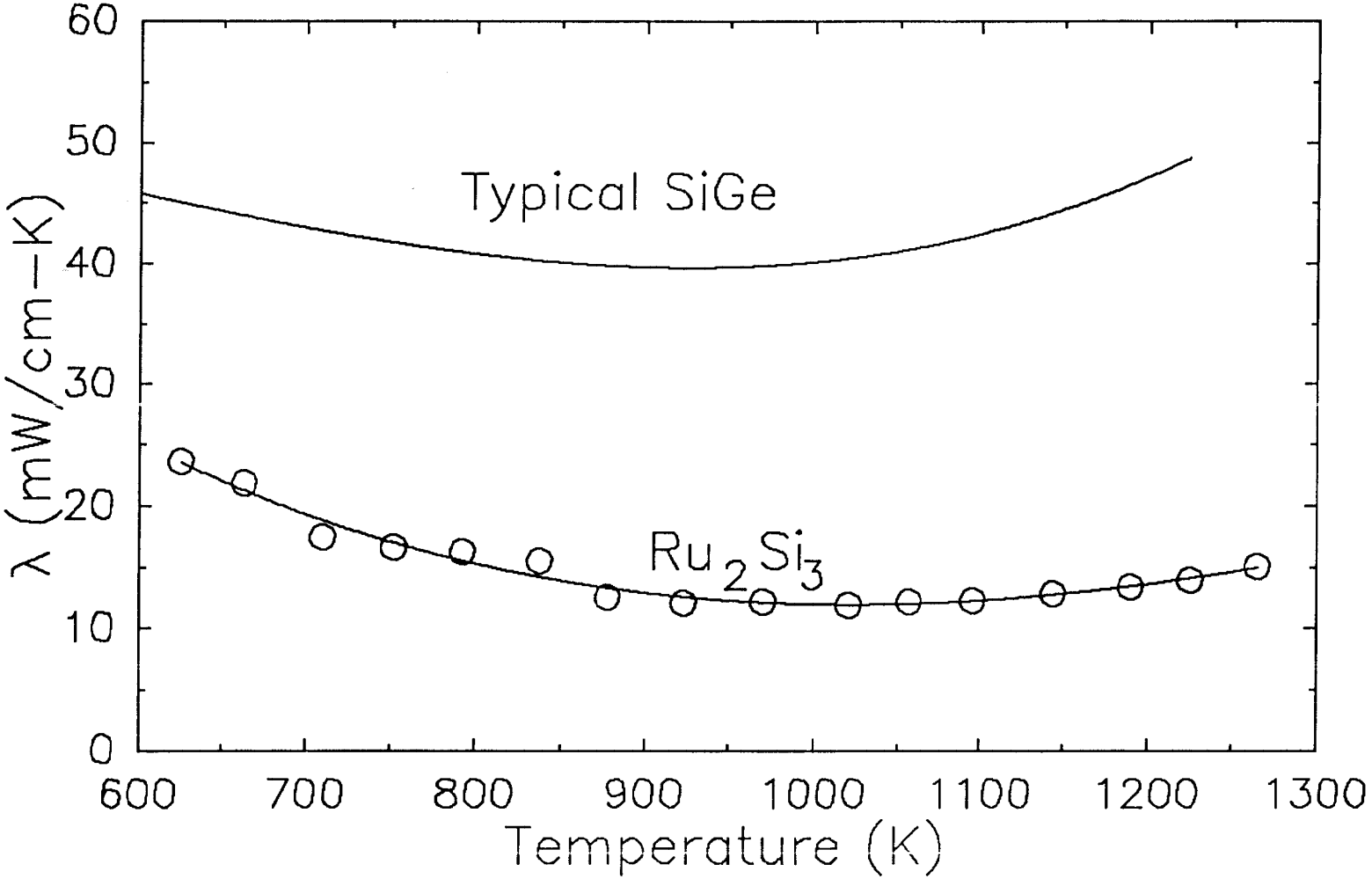
PREDICTED ZT FOR SILICIDES BASED ON SiGe MODEL



Electrical and Thermal Model For Advanced Materials



THERMAL CONDUCTIVITY REDUCTION FOR SILICIDES



THERMOELECTRIC PROPERTIES MODEL

CONCLUSIONS

- "TEXTBOOK" MODELS DESCRIBE SILICON-GERMANIUM ALLOYS REMARKABLY WELL
- $Z = 1 \times 10^{-3}\ K^{-1}$ IN N-TYPE SiGe/GaP IS CONSISTENT WITH HIGHER DOPING
- FURTHER IMPROVEMENTS IN Z BY DOPING ALONE ARE EXPECTED TO BE SMALL
- DRAMATIC IMPROVEMENTS IN Z ARE POSSIBLE
  - FOCUS ON REDUCED THERMAL CONDUCTIVITY

GLOSSARY OF TERMS AND EXPRESSIONS USED IN THE MODEL

CONSTANTS

e = magnitude of charge on an electron

m_e = mass of a bare electron

k_B = Boltzmann's constant

h = Plank's constant

$\hbar = h/2\pi$

N_A = Avagadro's Number

KNOWN MATERIAL PARAMETERS

y =	Germanium content ($Si_{1-y}Ge_y$)
$a^3 = (2.7155\ \text{Å})^3\ (1-y) + (2.8288\ \text{Å})^3\ y$	mean atomic volume
$\Delta a = 2.8288\ \text{Å} - 2.7155\ \text{Å}$	atomic size difference
$M = 28.086\ (1-y) + 72.59\ y$	mean atomic mass
$\Delta M = 72.59 - 28.086$	mass difference
$d = M/a^3$	mass density
$G = 1.033\ (1-y) + 1.017\ y$	related to elastic constants
$\theta = 4.19 \times 10^{-8}\ a^{-3/2}\ M^{-1/2}\ G$	Debye Temperature
$v = \frac{k_B}{\hbar}\ (6\pi^2)^{-1/3}\ \theta\ a$	speed of sound
$E_g = 0.8941 + 0.0421\ (1-y) + 0.1961\ (1-y)^2$ $- (0.00037\ y + 0.00023\ (1-y))\ *\ T$	band gap energy

β = 2.0, the ratio of Normal and Umklapp scattering rates

γ = 0.91 the anharmonicity parameter

MATERIAL PARAMETERS DETERMINED BY LEAST SQUARES FIT

$m\pm = 1.40\ m_e$	effective mass of a charge carrier in each band
$E_\pm = 2.94$ eV	deformation potential for each band
$\varepsilon\pm = 27.4$	dielectric constant for each band

CALCULATED MATERIAL PARAMETERS

$E_g^* = E_g/k_BT$ = reduced band gap energy

η = chemical potential of an electron (relative to conduction band edge)

$\eta^* = \eta/k_BT$ = reduced chemical potential

$n\pm$ = density of charge carriers in each band

$N_{a,d}$ = density of electron acceptors, donors

N = number density of atoms in the crystal

$\sigma\pm$ = partial electrical conductivity of each band

σ = total electrical conductivity

$R_H^{\pm}$ = partial Hall coefficient for each band

R_H = total Hall coefficient

$\mu_H^{\pm}$ = partial Hall mobility for each band

μ_H = total Hall mobility

$Q\pm$ = partial Seebeck coefficient for each band

Q = total Seebeck coefficient

$\mathcal{L}\pm$ = partial Lorentz factor for each band

$\mathcal{L}$ = total Lorentz factor

$K_e = \mathcal{L}\,\sigma\,T$ = electronic contribution to the thermal conductivity

K_ℓ = lattice contribution to the thermal conductivity

$K = K_e + K_\ell$ = total thermal conductivity

$ZT = Q^2\sigma T/K$ = thermoelectric figure of merit

$x = \mathcal{E}/k_BT$ = reduced energy of electrons or phonons

$E_\pm^* = \dfrac{\frac{1}{2}m\pm v^2}{k_B\,T}$ = Reduced carrier energy, at the speed of sound

$F_n(\eta^*)$ = Fermi integrals (n= 1/2 is the Fermi function)

$G_n^{\pm}(\eta^*)$ = Transport integrals

$H_n^{\pm}(\eta^*)$ = Transport integrals in a magnetic field

ELECTRICAL TRANSPORT COEFFICIENTS FOR

A SINGLE BAND OF HOLES

$$n^{+} = 4\,\pi \left(\frac{2\, m_{+}\, k_B\, T}{h^2} \right)^{3/2} F_{1/2}(-E_g^{*} - \eta^{*})$$

$$\sigma^{+} = \frac{8\,\pi\, e^2}{3\, m_{+}\, h^3} (2\, m_{+}\, k_B\, T)^{3/2}\, G_{+\,3/2}(-E_g^{*} - \eta^{*})$$

$$R_H^{+} = \frac{3\, h^3}{8\,\pi\, e\, (2\, m_{+}\, k_B\, T)^{3/2}} \frac{H_{+\,3/2}(-E_g^{*} - \eta^{*})}{G_{+\,3/2}^2(-E_g^{*} - \eta^{*})}$$

$$\mu_H^{+} = \frac{e}{m_{+}} \frac{H_{+\,3/2}(-E_g^{*} - \eta^{*})}{G_{+\,3/2}(-E_g^{*} - \eta^{*})}$$

$$Q^{+} = \frac{k_B}{e} \left[\frac{G_{+\,5/2}(-E_g^{*} - \eta^{*})}{G_{+\,3/2}(-E_g^{*} - \eta^{*})} + E_g^{*} + \eta^{*} \right]$$

$$\mathcal{L}^{+} = \left(\frac{k_B}{e} \right)^2 \left[\frac{G_{+\,3/2}(-E_g^{*} - \eta^{*})\, G_{+\,7/2}(-E_g^{*} - \eta^{*}) - G_{+\,5/2}^2(-E_g^{*} - \eta^{*})}{G_{+\,3/2}^2(-E_g^{*} - \eta^{*})} \right]$$

ELECTRICAL TRANSPORT COEFFICIENTS FOR

A SINGLE BAND OF ELECTRONS

$$n^- = 4\pi \left(\frac{2\, m^-\, k_B\, T}{h^2} \right)^{3/2} F_{1/2}(\eta^*)$$

$$\sigma^- = \frac{8\pi e^2}{3\, m^-\, h^3} (2\, m^-\, k_B\, T)^{3/2} G^-_{3/2}(\eta^*)$$

$$R_H^- = - \frac{3\, h^3}{8\pi e\, (2\, m^-\, k_B\, T)^{3/2}} \frac{H^-_{3/2}(\eta^*)}{G^{-2}_{3/2}(\eta^*)}$$

$$\mu_H^- = \frac{e}{m^-} \frac{H^-_{3/2}(\eta^*)}{G^-_{3/2}(\eta^*)}$$

$$Q^- = - \frac{k_B}{e} \left[\frac{G^-_{5/2}(\eta^*)}{G^-_{3/2}(\eta^*)} - \eta^* \right]$$

$$\mathcal{L}^- = \left(\frac{k_B}{e} \right)^2 \left[\frac{G^-_{3/2}(\eta^*)\, G^-_{7/2}(\eta^*) - G^{-2}_{5/2}(\eta^*)}{G^{-2}_{3/2}(\eta^*)} \right]$$

INTEGRALS FOR ELECTRICAL COEFFICIENT CALCULATIONS

$$F_n(\eta^*) = \int_0^\infty \frac{x^n\, dx}{1 + \exp(x-\eta^*)}$$

$$G^{\pm}_n(\eta^*) = \int_0^\infty \frac{\tau\pm\, x^n\, \exp(x-\eta^*)\, dx}{[1 + \exp(x-\eta^*)]^2}$$

$$H^{\pm}_n(\eta^*) = \int_0^\infty \frac{\tau\pm^2\, x^n\, \exp(x-\eta^*)\, dx}{[1 + \exp(x-\eta^*)]^2}$$

CHARGE CARRIER RELAXATION TIMES

$$\tau_{\pm} = \left(\tau_{\ell\pm}^{-1} + \tau_{i\pm}^{-1}\right)^{-1}$$

$$\tau_{\ell\pm} = \frac{\pi}{\sqrt{2}} \quad \frac{\hbar^4\, v^2\, M}{E_{\pm}^2\, a^3\, (m\pm\, k_B\, T)^{3/2}} \quad x^{-1/2}$$

$$\tau_{i\pm} = \frac{\sqrt{2\, m\pm}\ \varepsilon\pm^2}{\pi\, e^4\, (N_a + N_d)\, g\pm} \quad (k_B\, T)^{3/2} \quad x^{3/2}$$

$$g = \ln\left(1 + \frac{8\, m\pm\, k_B\, T}{\hbar^2} R_{\pm}^2\, x\right) - \frac{b\pm}{1 + b\pm}$$

$$R_{\pm}^{-2} = \frac{16\, \pi^2\, e^2\, m\pm^{3/2}\, (2\, k_B\, T)^{1/2}}{h^3\, \varepsilon\pm} F_{-1/2}(\eta^*)$$

$$b\pm = \frac{\varepsilon\pm\, h}{e^2} \left(\frac{2\, k_B\, T}{m\pm}\right)^{1/2}$$

ELECTRICAL TRANSPORT COEFFICIENTS FOR

A BAND OF HOLES PLUS A BAND OF ELECTRONS

$$Na + n- = Nd + n+$$

$$\sigma = \sigma+ + \sigma-$$

$$R_H = \left(R_H^+ \sigma_+^2 + R_H^- \sigma_-^2\right) / \sigma^2$$

$$\mu_H = \sigma R_H$$

$$Q = (Q^+\sigma^+ + Q^-\sigma^-) / \sigma$$

$$\mathcal{L} = \left(\mathcal{L}^+\sigma^+ + \mathcal{L}^-\sigma^- + \frac{\sigma^+\sigma^-}{\sigma}(Q^+ - Q^-)^2\right) / \sigma$$

$$K_e = \mathcal{L}\,\sigma\,T$$

LATTICE THERMAL CONDUCTIVITY

$$K_{\ell} = \frac{k_B}{2\,\pi^2\,v}\left(\frac{k_B\,\theta}{\hbar}\right)^3\left(I_1 + I_2^2/I_3\right)$$

USING:

$$I_1 = \int_0^{\theta/T} \tau_c \frac{x^4\,\exp(x)}{(\exp(x)-1)^2}\,dx$$

$$I_2 = \beta\int_0^{\theta/T} \frac{\tau_c}{\tau_U}\frac{x^4\,\exp(x)}{(\exp(x)-1)^2}\,dx$$

$$I_3 = \beta\int_0^{\theta/T} \frac{1}{\tau_U}\left(1 - \beta\frac{\tau_c}{\tau_U}\right)\frac{x^4\,\exp(x)}{(\exp(x)-1)^2}\,dx$$

PHONON RELAXATION TIME:

$$\tau_c^{-1} = (1+\beta)\,\tau_u^{-1} + \tau_{pd}^{-1} + \tau_e^{-1}$$

$$\tau_u^{-1} = \frac{20\,\pi}{3}\hbar\,N_A\left(\frac{6\,\pi^2}{4}\right)^{1/3}\frac{1+\frac{5}{9}\beta}{1+\beta}\frac{\gamma^2}{M\,a^2}\left(\frac{T}{\theta}\right)^3 x^2$$

$$\tau_{pd}^{-1} = y\,(1-y)\left[(\Delta M/M)^2 + 39\,(\Delta a/a)^2\right]\left(\frac{a}{v}\right)^3\left(\frac{k_B\,T}{\hbar}\right)^4 x^4$$

$$\tau_e^{-1} = \frac{E_{\pm}^2\,m_{\pm}^3\,v}{4\,\pi\,\hbar^4\,d\,E_{\pm}^*}\ln\left(\frac{1+\exp(-E_{\pm}^* + \eta^* - x^2/16\,E_{\pm}^* + x/2)}{1+\exp(-E_{\pm}^* + \eta^* - x^2/16\,E_{\pm}^* - x/2)}\right)$$

A MODEL FOR THE THERMOELECTRIC PROPERTIES OF N-TYPE SILICON-GERMANIUM ALLOYS

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INTRODUCTION

Silicon-germanium alloys have proven remarkably reliable in Radioisotope Thermoelectric Generators (RTGs) and are the current materials of choice for the SP-100 space reactor program. However, even after three decades of study and extensive practical experience (including the spectacular Voyager missions) the best available models of the thermoelectric properties of these materials are little more than interpolation schemes based on experimental data. The present study extends a previous model for the thermal conductivity and, for the first time, applies conventional transport theory to develop a model for the electrical properties of n-type silicon germanium. Moreover, it is shown that treating the electrical and thermal models self-consistently predicts the observed properties of silicon-germanium with good accuracy using only three, physically interpretable parameters. The nature of the model and agreement with experiment are discussed.

BACKGROUND

Ideally, the efficiency of a thermoelectric system can be calculated from a knowledge of a single material property: the dimensionless thermoelectric figure of merit, ZT. ZT is related to measurable materials parameters by $ZT=Q^2\sigma T/\lambda$, where Q is the Seebeck coefficient, σ is the electrical conductivity and k is the thermal conductivity.

Silicon and germanium, the two most intensely studied semiconductors, possess small ZT values, perhaps 0.1-0.2 and are nearly useless for thermoelectric applications, in spite of attractive chemical and mechanical properties. Heavily doped, n-type alloys of silicon and germanium, however, achieve ZT values around 1.0 (Dismukes et al, 1964) due to a reduction in the thermal conductivity upon alloying and have been the materials of choice for thermoelectric space power systems since their development over 20 years ago.

To understand the behavior of ZT as a function of composition, doping level and temperature a model of the thermoelectric properties is needed. The conventional theory of the simultaneous transport of electrical charge and heat in a solid, a rich subject filled with assumptions (which will not be discussed here), provides the following picture. A solid consists of a nearly regular geometric arrangement of atoms, called a lattice, which vibrate around their equilibrium sites. Since each atom is bonded to the its neighbors, the displacement of one atom is not independent of the displacement of its neighbors. Motion of an atom at one site will cause neighboring atoms to move also. Hence, a disturbance at one site will propagate throughout the lattice, much like the waves on a pond in which a pebble has been dropped.

Since these "waves" of propagation in a lattice are the mechanism by which

sound travels through a solid, they have been called phonons and are characterized by their frequency and the speed with which they propagate, i.e. the speed of sound, v. Each phonon (loosely, a particle of sound) carries energy in the direction of propagation, in just the same way that a photon (a particle of light) carries energy. Occasionally, a phonon will hit something which alters its energy and momentum. These are called scattering events and are characterized by the scattering rate, given by $1/\tau_{ph}$, which represents the number of scattering events per second. The typical phonon travels some typical distance, $l_{ph} = v\,\tau_{ph}$. The heat carried by the typical phonon is just the heat capacity, C_{ph}. A crude estimate of the thermal conductivity of the lattice is then given by $k_{ph} = \frac{1}{3} C_{ph} v\, l_{ph}$.

So far, our solid is an electrical insulator, since only the motion of the (neutral) atoms have been considered. Consider that a few of the atoms are different most and have one more electron around the nucleus than their neighbors. These few atoms are called dopants. The extra electrons travel about essentially freely through the solid and are called conduction electrons. Just like the phonons, these electrons will occasionally be scattered (hit something) altering their energy and momentum and the scattering rate for electrons is given by $1/\tau_{el}$. The electrical conductivity is given by $\sigma = n\, e^2\, \tau_{ph}/m$. And, using the Wiedemann-Franz law, the electronic thermal conductivity is given by $k_{el} = \mathcal{L}\, \sigma\, T$, where $\mathcal{L}$ is a constant. Thus, the total thermal conductivity, k, consists of the sum of an electronic component and a lattice component.

The Seebeck coefficient is more complex than either of the conductivities. For illustrative purposes the approximation $Q = \frac{k}{e} \ln (n/n_0)$, where n is the carrier concentration and n_0 is a parameter which depends on temperature and the scattering mechanism, is useful. $\frac{k}{e}$ is the ratio of Boltzmann's constant to the charge of the electron and has the value 86 μV/K. This expression shows that the Seebeck tends to be large and negative (for n-type) at low carrier concentrations and tends to approach zero as n approaches n_0 from below, exactly as observed experimentally in silicon-germanium alloys.

While the expressions given here for σ, k and Q are exceedingly crude, they never-the-less capture much of the important physics of thermoelectric materials. In order to turn these expressions into useful, predictive tools several things must be done. First, the important electron and phonon scattering mechanisms need to be identified and expressions for the scattering rates derived. Second, since the scattering rates will depend on the energy of the particles, averaging techniques need to be developed. And finally, the values of the appropriate parameters need to be identified.

Fortunately, the first two tasks have been essentially done in the literature. The scattering mechanisms and averaging techniques for calculating the lattice thermal conductivity has been well described (Steigmeier and Abeles, 1964). The important scattering mechanisms for phonons are: scattering by other phonons; scattering by point defects (due alloying silicon with germanium); and scattering by electrons.

The possible scattering mechanisms and appropriate averaging techniques for

the electrical properties (σ, Q and k_{ph}) are also well described in the literature (Fistul', 1969). The important scattering mechanisms for electrons are: scattering by the dopant atoms themselves; and scattering by phonons.

A great many effects have been ignored in these two models. One goal of this study is to determine the extent to which these relatively simple models can describe the observed properties of silicon-germanium alloys. Since the models themselves are well established, the only remaining task is to determine the appropriate values for the parameters.

Parameters describing phonon scattering by other phonons and scattering by point defects (alloy scattering) have been taken from the literature (Steigmeier and Abeles, 1964). These parameters were determined by study of the thermal conductivity of pure silicon and undoped silicon-germanium alloys. In order to describe the scattering of phonons by electrons the same authors used Ziman's expression for the phonon-electron scattering rate, which involves two unknown parameters: the effective mass of the electron and the deformation potential. In order to achieve a good description of the data, Steigmeier and Abeles allowed the deformation potential to vary with doping level. This procedure considerably weakens the utility of the model, while still suggesting that the basic model is not entirely wrong.

In order to estimate the lattice thermal conductivity of a doped material, one must subtract the electronic contribution from the total thermal conductivity. This procedure is not so easy to perform since first one must have a reasonably reliable model for the electrical properties. Regarding the samples composition and doping level as known, only three unknown parameters need be determined to calculate the electrical properties:

m,	effective mass of the electron
Ξ,	deformation potential.
ε,	dielectric constant

A great many other parameters are also required, but they are either known from other measurements or can be calculated. Hence, once the electrical model is completed, the lattice thermal conductivity is also be determined with no additional parameters.

COMPARISON OF MODEL AND EXPERIMENTAL RESULTS

Best fit values for m, Ξ and ε were determined using a least squares routine. Experimental data on σ, Q, the Hall mobility and k for about a dozen n-type silicon-germanium alloys, covering room temperature doping levels between about 10^{18} to 2×10^{20}, germanium contents between 0 and 40% and temperatures between 300 K and 1300 K. Comparison of some experimental and calculated values for $\rho = 1/\sigma$, Q and 1/k are shown in Figures 1 through 3, where the solid lines represent the model calculations. The agreement is seen to be quite good.

It should be emphasized that only three adjustable parameters are involved in this model. This is the first physically plausible model of the electrical properties of silicon-germanium. Also, the thermal conductivity model represents a significant improvement over the previous model, in that a single deformation potential value is sufficient over the entire doping range of interest.

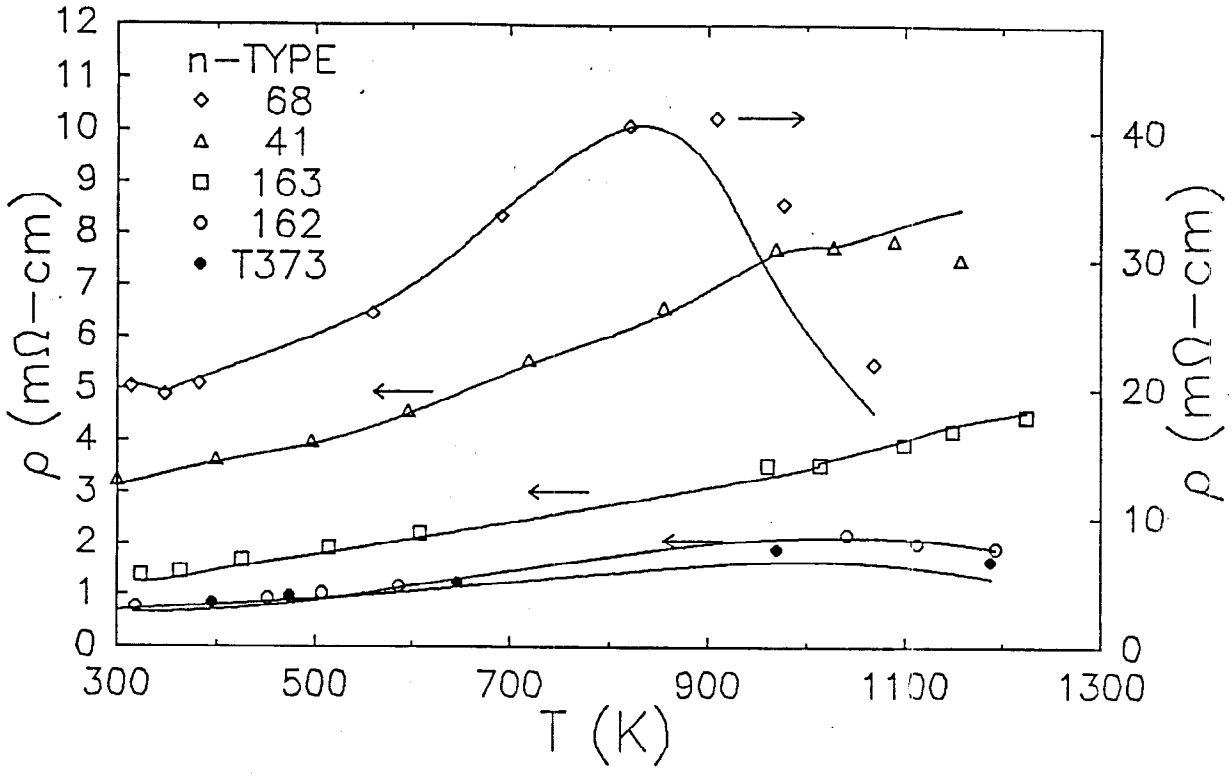

Figure 1. The electrical resistivity for five samples of silicon-germanium as a function of temperature. Solid lines represent the model calculations.

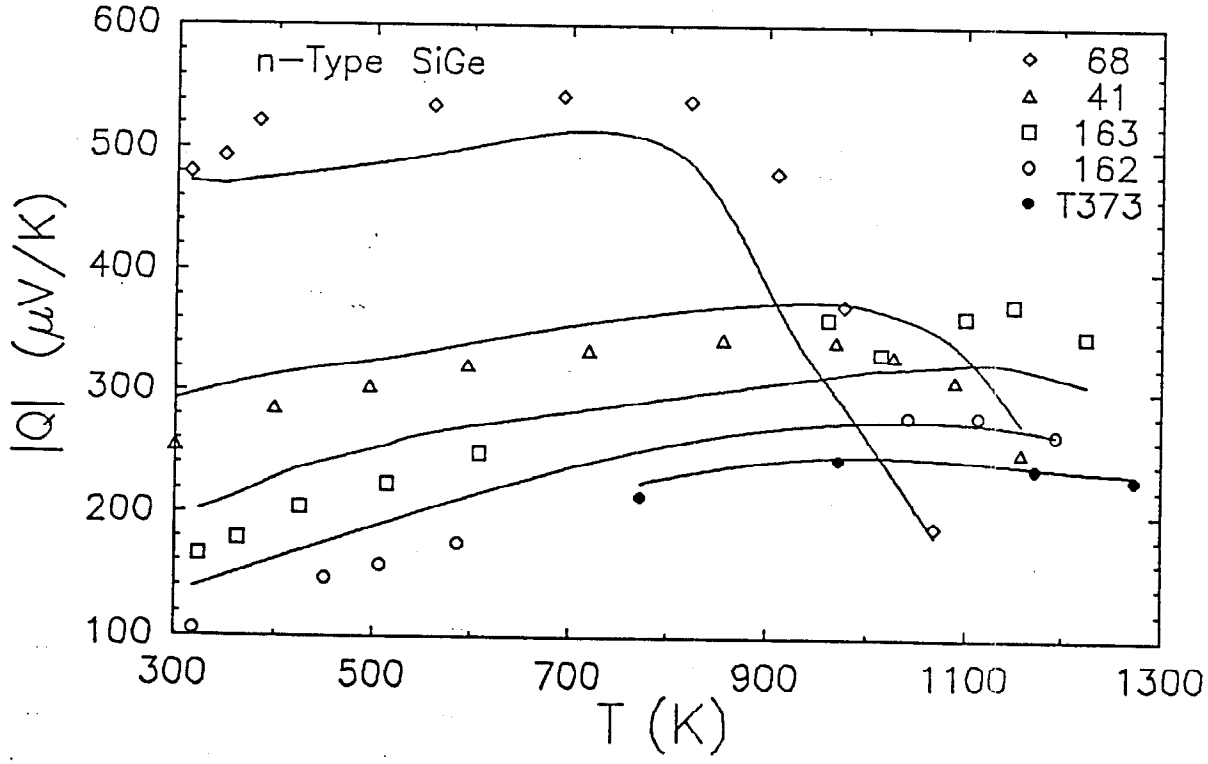

Figure 2. The Seebeck coefficient for five samples of silicon-germanium as a function of temperature. Solid lines represent the model calculations.

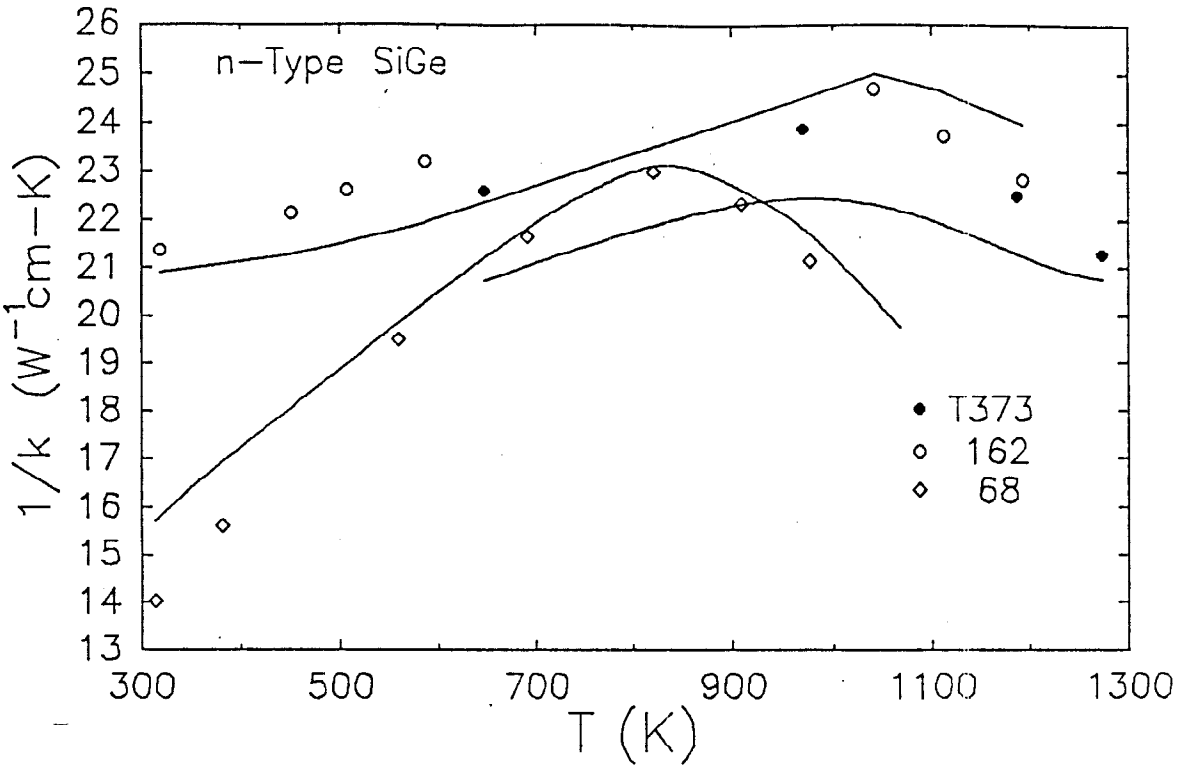

Figure 1. The thermal conductivity for three samples of silicon-germanium as a function of temperature. Solid lines represent the model calculations.

CONCLUSIONS

This study establishes for the first time that conventional thermoelectric theory is sufficient to provide an accurate and quantitative description of all of the transport properties of silicon-germanium alloys. Moreover, excellent agreement with experiment is achieved with only a minimum number of adjustable parameters.

Extrapolation of the results of this model beyond the regimes where experimental data are available is now underway and is expected to be a key factor in the development of significantly improved thermoelectric materials.

Acknowledgements

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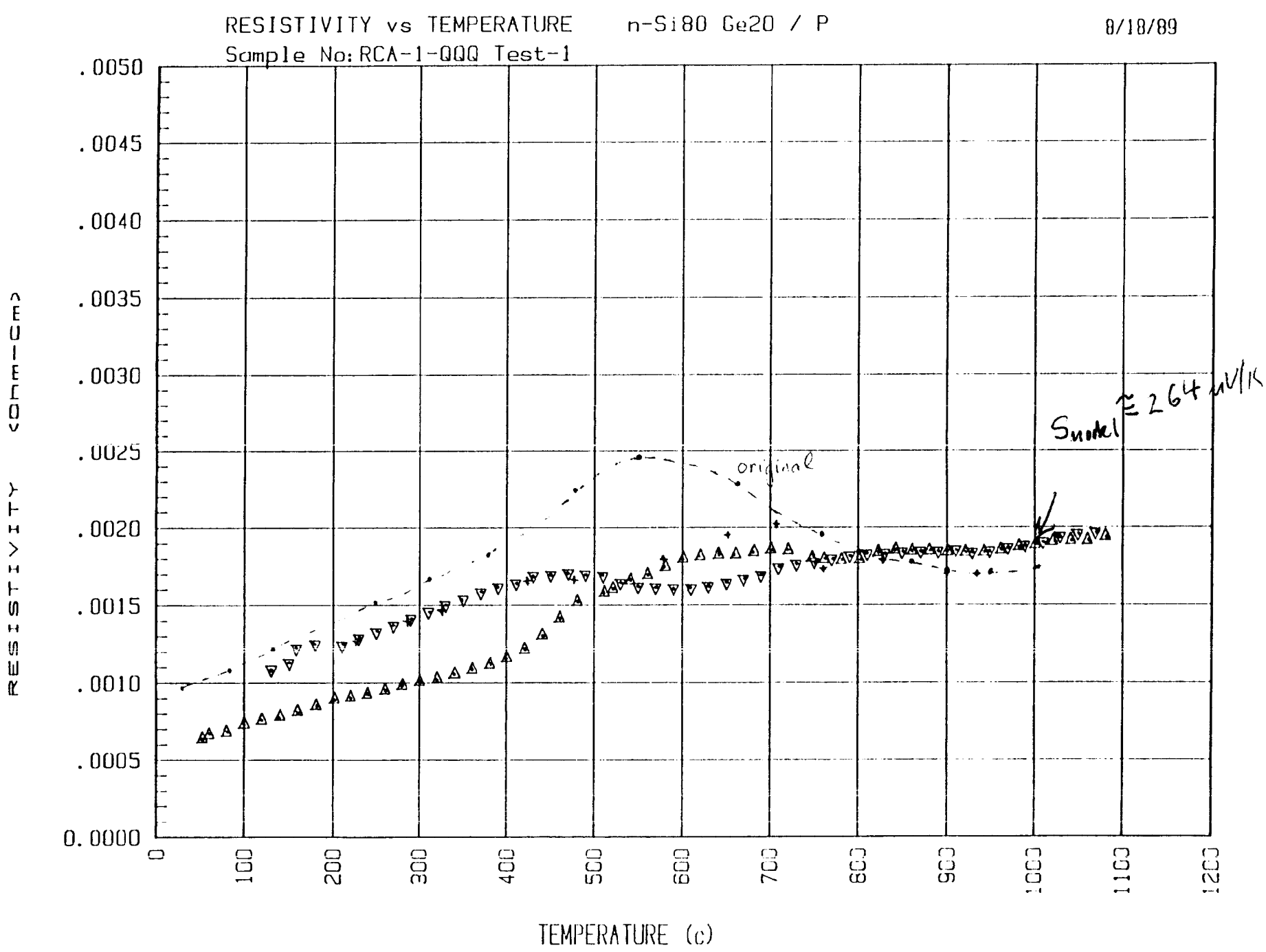
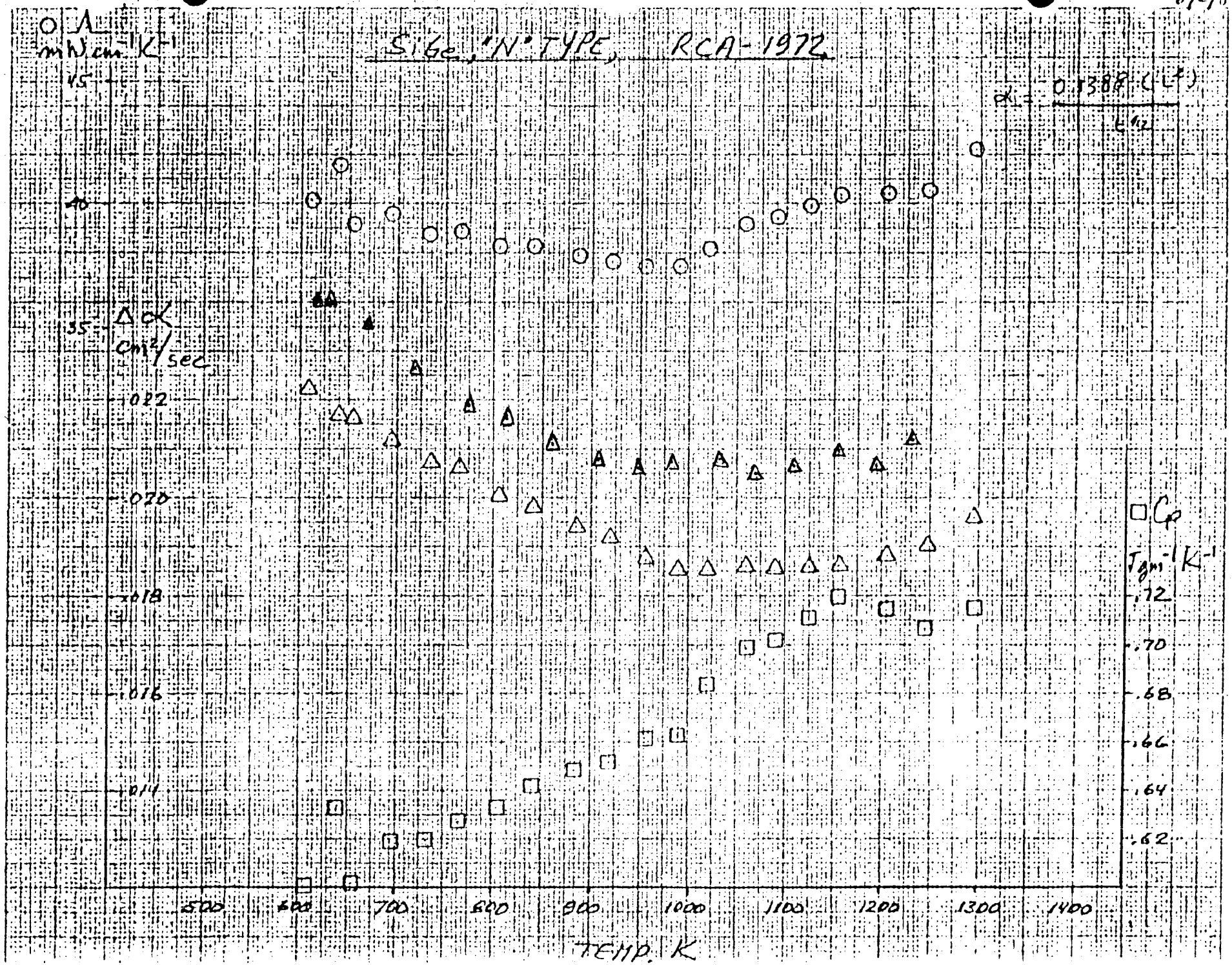
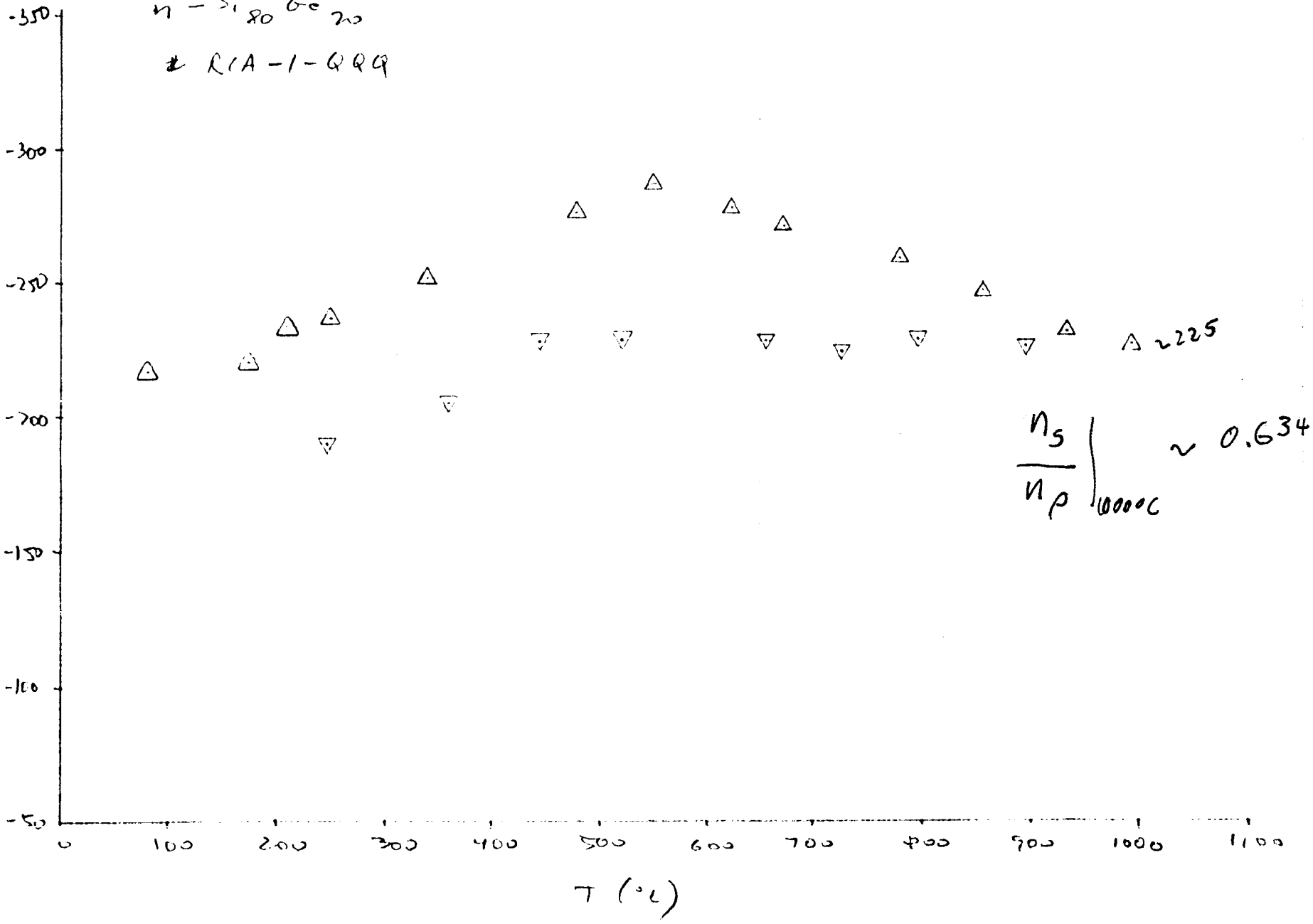

RESISTIVITY vs TEMPERATURE n-Si80 Ge20 / P
8/18/89
Sample No: RCA-1-QQQ Test-1
RESISTIVITY (OHM-CM)
.0050
.0045
.0040
.0035
.0030
.0025
.0020
.0015
.0010
.0005
0.0000
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
TEMPERATURE (c)
original
Slope ≅ 264 mV/K

6/2/80


Si Ge, 'N' TYPE, RCA-1972
λ mW cm⁻¹ K⁻¹
α = 0.1388 (L²/L/2)
ΔK cm²/sec
Cp Jgm⁻¹ K⁻¹
45
40
35
.022
.020
.018
.016
.014
.72
.70
.68
.66
.64
.62
500
600
700
800
900
1000
1100
1200
1300
1400
TEMP. K


n – Si80Ge20
RIA-1-QQQ
-350
-300
-250
-200
-150
-100
-50
0
100
200
300
400
500
600
700
800
900
1000
1100
T (°C)
S (μV/K)
▽ ~225
$\frac{n_s}{n_p}\Big|_{1000°C} \sim 0.634$

T373

Estimated, interpolated from data

T(°C)	ρ	PF	λ	ZT
500	1.228	36	45	0.618
600	1.374	38.4	42	0.798
700	1.487	~~41.1~~ 38.9	40.1	0.944
800	1.433	~~41.0~~ 41.1	40.9	1.078
900	1.356	41.0	42.4	1.134
1000	1.294	40.34	44.4	1.157

K	ρ	N	ZT
800	1.267	1.594	0.667
1050	1.445	1.831	1.047
1300	1.279	2.703	1.162