

International Cryogenics Monograph Series

Guglielmo Ventura  
Mauro Perfetti

# Thermal Properties of Solids at Room and Cryogenic Temperatures

 Springer

# **International Cryogenics Monograph Series**

*Series editor*

Steven W. Van Sciver, Florida State University, Tallahassee, FL, USA

For further volumes:  
<http://www.springer.com/series/6086>

The International Cryogenics Monograph Series was established in the early 1960s to present an opportunity for active researchers in various areas associated with cryogenic engineering to cover their area of expertise by thoroughly covering its past development and its present status. These high level reviews assist young researchers to initiate research programs of their own in these key areas of cryogenic engineering without an extensive search of literature.

Guglielmo Ventura · Mauro Perfetti

# Thermal Properties of Solids at Room and Cryogenic Temperatures

 Springer

Guglielmo Ventura  
INFN  
Roma  
Italy

Mauro Perfetti  
Dipartimento di Chimica  
Università di Firenze  
Sesto Fiorentino  
Italy

ISSN 0538-7051                      ISSN 2199-3084 (electronic)  
ISBN 978-94-017-8968-4            ISBN 978-94-017-8969-1 (eBook)  
DOI 10.1007/978-94-017-8969-1  
Springer Dordrecht Heidelberg New York London

Library of Congress Control Number: 2014941685

© Springer Science+Business Media Dordrecht 2014

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed. Exempted from this legal reservation are brief excerpts in connection with reviews or scholarly analysis or material supplied specifically for the purpose of being entered and executed on a computer system, for exclusive use by the purchaser of the work. Duplication of this publication or parts thereof is permitted only under the provisions of the Copyright Law of the Publisher's location, in its current version, and permission for use must always be obtained from Springer. Permissions for use may be obtained through RightsLink at the Copyright Clearance Center. Violations are liable to prosecution under the respective Copyright Law. The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

While the advice and information in this book are believed to be true and accurate at the date of publication, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Printed on acid-free paper

Springer is part of Springer Science+Business Media ([www.springer.com](http://www.springer.com))

*To Eva and other demons*

Guglielmo Ventura

*If I were a metal, I would definitely say  
that I am a heavy lanthanide.*

*When the temperature is lowered enough  
with a powerful refrigerator (Guglielmo),  
and a strong magnetic field is applied  
(Roberta) my domains (Sergio, Antonella,  
Sandro) cooperatively align themselves  
to create a strong ferromagnet.*

*When another magnet (Eva) is sufficiently  
near me, we can interact and cooperate  
with other magnets (the LaMM staff) to  
create an even stronger material*

Mauro Perfetti

# Preface

This book addresses the needs of researchers in physics and chemistry, project engineers and students interested in cryogenics and thermal properties of matter. Using a musical analogy it is piano four hands, not a work for two different instruments. The book's three parts, each of which is devoted to a respective thermal property, are written with the same guiding philosophy: (1) to describe theories on the propagation of heat in solids in a format that is concise but sufficiently detailed to understand the three thermal phenomena; (2) to review the main experimental techniques with some examples taken from the literature; and (3) to present experimental data in the form of tables and graphs.

A rich bibliography is provided at the end of each chapter.

*Scientists* will be particularly interested in the measurements methods, which describe some important details in set-ups at cryogenic temperatures. In addition, data on the thermal properties of several materials at the low (4–300 K) and very low (<4 K) temperature range are provided at the end of each Part.

For *Project Engineers* data on the three thermal properties and the integrated data in the form of tables will offer an essential and time-saving resource.

*Students* will be provided with the basics for performing measurements at low temperatures, and with a general, concise guide to the theory involved, focusing on the most important formulas and concepts necessary for understanding the thermal properties of solids at low temperatures.

For the sake of conciseness, the words “materials solid at standard temperature and pressure (stp)” were omitted from the title. Of course any material will become solid when the temperature is lowered and/or pressure is increased: for example  ${}^4\text{He}$  becomes solid below  $T \approx 2 \text{ K}$  under a pressure  $\geq 25 \text{ bar}$ .

Only a few materials not solid at stp (e.g. noble gases) are examined, in Part I. Though data on these materials is often of considerable interest (consider e.g. the importance of solid nitrogen enthalpy), it would go beyond the scope of this book.

Guglielmo Ventura  
Mauro Perfetti

# Contents

## Part I Heat Capacity

<b>1 Heat Capacity</b> . . . . .	3
1.1 Introduction. . . . .	3
1.2 Lattice Specific Heat . . . . .	6
1.3 Electronic Specific Heat . . . . .	9
1.4 Electronic Specific Heat in Superconducting Materials. . . . .	11
1.5 Specific Heat Contributions from Transitions and Defects. . . . .	14
1.6 Magnetic Specific Heat. . . . .	17
1.6.1 Magnetic Order and Specific Heat. . . . .	17
1.6.2 The Schottky Anomaly. . . . .	20
1.6.3 Materials Used for Magnetic Refrigeration . . . . .	24
1.6.4 Heat Capacity of Regenerators for Cryocoolers. . . . .	25
1.7 Specific Heat Due to the Amorphous State . . . . .	28
1.8 Conclusion . . . . .	32
References . . . . .	32
<b>2 How to Measure Heat Capacity at Low Temperatures</b> . . . . .	39
2.1 Introduction. . . . .	39
2.2 Calorimeters . . . . .	41
2.3 Heat Pulse Calorimetry. . . . .	44
2.3.1 Example 1: Heat Pulse Calorimeter for a Small Sample at Temperatures Below 3 K . . . . .	44
2.3.2 Example 2: Heat Pulse Calorimetry for the Measurement of the Specific Heat of Liquid $^4\text{He}$ Near its Superfluid Transition. . . . .	47
2.4 Relaxation Calorimetry. . . . .	48
2.4.1 Example: Measurement of Specific Heat of Heavily Doped (NTD) Ge. . . . .	50
2.5 Dual Slope Method . . . . .	52
2.6 AC Calorimetry . . . . .	55
2.7 Differential Scanning Calorimetry . . . . .	57
2.8 Other Methods. . . . .	59
2.9 Industrial Calorimeters . . . . .	60



2.10	Small Sample Calorimetry . . . . .	61
	References . . . . .	63
<b>3</b>	<b>Data of Specific Heat . . . . .</b>	<b>69</b>
3.1	Presentation of DATA of Specific Heat . . . . .	69
3.2	Very-Low Temperature DATA (Below About 4 K) . . . . .	69
3.2.1	Metals and Alloys . . . . .	69
3.2.2	Dielectrics . . . . .	70
3.3	Low-Temperature Specific Heat DATA (Approximately 4–300 K) . . . . .	72
3.3.1	Metals and Alloys . . . . .	72
3.3.2	Dielectrics . . . . .	72
	References . . . . .	77
 <b>Part II Thermal Expansion</b>		
<b>4</b>	<b>Thermal Expansion . . . . .</b>	<b>81</b>
4.1	Introduction. . . . .	81
4.2	Thermal Expansion Theory . . . . .	82
4.3	Negative Thermal Expansion. . . . .	86
4.3.1	Application of NTE . . . . .	86
	References . . . . .	88
<b>5</b>	<b>How to Measure the Thermal Expansion Coefficient at Low Temperatures. . . . .</b>	<b>93</b>
5.1	Capacitive Dilatometers . . . . .	94
5.1.1	Principles of Capacitive Techniques. . . . .	94
5.1.2	Examples . . . . .	96
5.2	Interferometric Dilatometers . . . . .	102
5.2.1	Principles of Interferometric Dilatometry . . . . .	103
5.2.2	Homodyne Dilatometer: Example . . . . .	106
5.2.3	Heterodyne Dilatometer with Cryogenic Liquids: Examples . . . . .	107
5.2.4	Heterodyne Interferometric Dilatometer: Example . . . . .	111
5.2.5	Heterodyne Dilatometer with Mechanical Coolers: Examples. . . . .	116
5.3	Very Low Temperature Thermal Expansion . . . . .	117
	References . . . . .	118
<b>6</b>	<b>Data of Thermal Expansion . . . . .</b>	<b>121</b>
	References . . . . .	127

**Part III Thermal Conductivity**

**7 Electrical and Thermal Conductivity** . . . . . 131

7.1 Electrical Conductivity . . . . . 131

7.1.1 Relation Between Thermal and Electrical  
Conductivity . . . . . 131

7.1.2 Electrical Resistivity of Metals . . . . . 134

7.1.3 Electrical Conductivity of Semiconductors . . . . . 137

7.2 Magnetic and Dielectric Losses . . . . . 139

7.2.1 Losses in Dielectric Materials . . . . . 139

7.3 Thermal Conductivity . . . . . 141

7.3.1 Introduction . . . . . 141

7.3.2 Lattice Thermal Conductivity . . . . . 145

7.3.3 Thermal Conductivity of Dielectrics . . . . . 146

7.3.4 Thermal Conductivity of Nanocomposites . . . . . 152

7.3.5 Composite Materials . . . . . 155

References . . . . . 162

**8 How to Measure Thermal Conductivity** . . . . . 169

8.1 Introduction . . . . . 169

8.2 Steady State Techniques . . . . . 170

8.2.1 Longitudinal Flux Method . . . . . 171

8.2.2 Radial Flux Method or Cylinder Method . . . . . 173

8.3 Transient Methods . . . . . 174

8.3.1 The  $3\omega$  Method . . . . . 174

8.3.2 Pulse Power Method . . . . . 177

8.4 Thermal Diffusivity Measurements . . . . . 179

8.4.1 Laser Flash Method . . . . . 179

8.4.2 Temperature Wave Method . . . . . 180

8.5 Examples of Measurements of Electrical  
and Thermal Conductivity . . . . . 181

8.5.1 Measurement of Electrical Resistivity of Heavily  
Doped NTD 31 Germanium at Very Low  
Temperatures, and Calculation of Electron-phonon  
Decoupling . . . . . 181

8.5.2 Measurement of the Thermal Conductivity  
of Torlon in the 0.08–300 K Temperature Range . . . . . 185

References . . . . . 190

**9 Data of Thermal Conductivity** . . . . . 195

9.1 Very Low Temperature Data . . . . . 195

9.2 Low Temperature Data . . . . . 195

9.3 Crystalline Materials . . . . . 213

References . . . . . 213

# Part I

## Heat Capacity

### Main Symbols

$Q$	Heat flow
$C$	Heat capacity
$c$	Specific heat
$T$	Temperature
$E$	Internal energy
$V$	Volume/molar volume
$S$	Entropy/Total spin momentum
$p$	Pressure
$c_V$	Constant volume specific heat
$c_p$	Constant pressure specific heat
$\beta$	Coefficient of volume thermal expansion
$\gamma_G$	Grüneisen parameter
$\zeta_T$	Isothermal compressibility coefficient
$\zeta_S$	Adiabatic compressibility coefficient
$\theta_D$	Debye temperature
$N_A$	Avogadro's constant
$k_B$	Boltzmann's constant
$h$	Plank's constant
$R$	Ideal gas constant/resistance
$\rho$	Density
$M_m$	Molar mass
$v$	Velocity
$g$	Volumetric density of states
$E_F$	Fermi energy
$\gamma$	Sommerfeld's constant
$r$	Number of atoms per molecule
$L$	Latent heat/orbital angular momentum
$H$	Magnetic field/enthalpy/heater
$G$	Gibbs free energy
$\chi$	Magnetic susceptibility

$P$	Power
$t$	Time
$\kappa$	Thermal conductivity
$R$	Thermal resistance
$F$	de Gennes factor
$J$	Total angular momentum
$a$	Radial distance from a given ion

# Chapter 1

## Heat Capacity

**Abstract** Specific heat provides a link among the many solid state theories; vice versa these theories can also be used to estimate the specific heat of materials. From a practical point of view, the knowledge of the specific heat of technically important materials is often fundamental in the design of instruments and systems which have to work in the low temperature regime. Since cryogenics is presently used in research, aerospace, industry and energy production and storage, specific heat data for commonly used materials are mandatory. In this chapter theories about contributions to specific heat are reported: lattice specific heat (Sect. 1.2), electronic specific heat in normal (Sect. 1.3) and superconducting (Sect. 1.4) materials, contributions from transitions and defects (Sect. 1.5), magnetic specific heat (Sect. 1.6), contributions present in amorphous materials (Sect. 1.7).

### 1.1 Introduction

Specific heat,  $c$ , is an intensive variable that relates the heat per unit mass supplied to a system to the resultant absolute temperature change of the system itself. Several needs have stimulated the study of this thermal property of matter. In fact, specific heat experiments verified Nernst's statement of the third law of thermodynamics, allowed the calorimetric determination of the energy states of substances and were the basis for Greywall's study about  $^3\text{He}$  melting pressure thermometry.

Specific heat provides a link among the many solid state theories; conversely, these theories can be used to estimate the specific heat of materials. From a practical point of view, the knowledge of the specific heat of technically important materials is often fundamental in the design of instruments and systems which have to work in the low temperature regime. Since cryogenics is presently used in research, aerospace, industry and energy production and storage, specific heat data for commonly used materials are mandatory. Most low temperature specific heat data refer to very pure samples (difficult to obtain) or exotic compounds; hence, needed

values must be computed from very limited data. Calculation and estimation of specific heats are sometimes possible by using accepted models [1]. Predictions on the specific heat of particular materials, e.g., have been reported [2–4].

Luckily, when the temperature is reduced, the thermal properties of materials often become easier to describe (solid  $^3\text{He}$  is one of the few exceptions). In particular, the various contributions to the specific heat of a material can be studied independently: for example, the contribution which originates from the nuclear spin can be considered independent from the electron and phonon systems. Moreover, the electron and phonon contribution of a metal can be simply added to obtain the total specific heat. However, this is not always true; in fact it is usually impossible to calculate the specific heat of superconducting alloys from the knowledge of the various components' specific heat. Rigorous developments of theories about the various contributions to the specific heat can be found in many books on solid-state physics [5–13]. Here, we present the principal models which explain the underlying physics of each contribution in a concise form.

Heat capacity,  $C$ , is defined as the amount of heat,  $dQ$ , required to raise the temperature of a material by a unit of temperature:

$$C_x = \left[ \frac{dQ}{dT} \right]_x \quad (1.1)$$

where  $x$  denotes any of the several constraints which can be imposed. The most common constraints are pressure ( $p$ ) and volume ( $V$ ). Contrarily to specific heat, heat capacity is an extensive quantity, which means that it depends on the size of the system.

As many other physical properties, the heat capacity can be defined in terms of other thermodynamic state variables, in particular, it can be written as the derivative of either the entropy,  $S$ , or internal energy,  $E$ , as

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V. \quad (1.2)$$

Equation (1.2) indicates that when the temperature of a system is increased but the system is forced to maintain a constant volume, all the heat is stored as internal energy. Likewise, constant pressure heat capacity may be written as

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P = \left( \frac{\partial E}{\partial T} \right)_P + P \left( \frac{\partial V}{\partial T} \right)_P \quad (1.3)$$

where  $H$  is the enthalpy. It is also possible to define  $C$  with other external variables held constant. For example, in systems with relevant magnetic properties,  $C_H$  or  $C_M$  may be used to designate the heat capacity at a constant applied magnetic field or magnetization, respectively. This topic is of particular interest in magnetic cooling systems (see Sect. 1.6) [14]. Among the several systems of units often used to express specific heat, we shall adopt  $\text{J mol}^{-1} \text{K}^{-1}$ , except in the case of

alloys or nonstoichiometric compounds, where mass is more appropriate than molar basis. Hence,

$$c_x = \frac{1}{n} \left[ \frac{dQ}{dT} \right]_x \quad (1.4)$$

where  $n$  is the number of moles. Let us note that in some applications, it is useful to define a heat capacity per unit volume. In order to avoid misunderstanding, we will remark “per unit volume” every time that this quantity is present in equations.

To evaluate the specific heat, the various excitations that take place in the examined material are to be considered. To do that, an accurate chemical analysis of the studied sample itself is mandatory because impurities and defects can play a crucial role at very low temperatures. The chemical structure of the materials is strictly connected to the ways in which the heat is propagated through the materials. Thus, as mentioned, the specific heat gives plenty of information about the specimen.

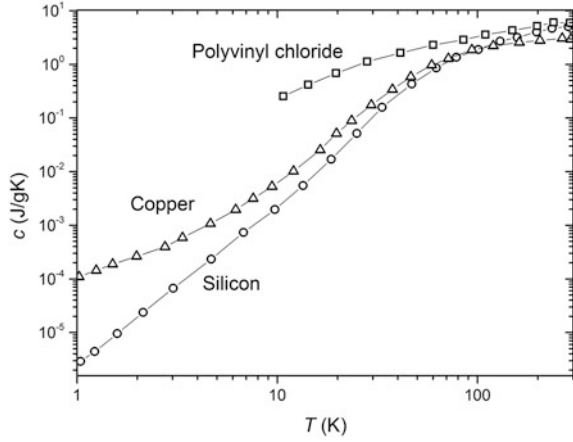
Note that experimental data usually give the specific heat at constant pressure  $c_p$  because of the practical difficulty of keeping the volume constant. Instead, theories usually refer to the specific heat at the constant volume  $c_v$  parameter which does not take into account the thermal expansion (see Part II). This is why the specific heat  $c_p$  is always greater than  $c_v$ , by a factor  $(1 + \beta\gamma_G T)$ , where  $\beta$  is the volumetric coefficient of thermal expansion and  $\gamma_G$  is the so-called Grüneisen parameter defined as

$$\gamma_G = \beta \frac{V}{\zeta_T c_V} = \beta \frac{V}{\zeta_S c_P} \quad (1.5)$$

where  $V$  is the molar volume and  $\zeta_T$  and  $\zeta_S$  are the isothermal and adiabatic compressibility coefficients (see Sect. 1.5 and Part II, Sect. 4.2) [5–13].

For most solids below room temperature,  $c_p$  exceeds  $c_v$  by less than 2 % (about 1 % at  $T = \theta_D/2$ , with  $\theta_D$  the Debye temperature of the material). This little difference is due to the fact that  $\beta$  is extremely small below  $\theta_D$  (see Part II, Sect. 4.2 for further details). The latter consideration allows one to discuss how  $c_v$ , studied in theoretical models, [5–13] depends on temperature, and to compare it with experimental data of  $c_p$ . In fact, a fairly extensive amount of experimental data of  $c_p$  exists for solids at room and low-temperatures. For simple solids such as metals and crystalline insulators, there is a good match between experimental and theoretical data near room temperature. The classical model of harmonic oscillators developed by Dulong and Petit [15] works well around room temperature. Adopting this model, the heat capacity (independently from temperature and type of material) is 25 J/mol K for a monoatomic solid. At low temperatures,  $c_p$  is temperature dependent and there is a markedly different behavior according to the type of solid, as we shall see in the following sections, where the phenomena which contribute to the specific heat are separately considered. Note that to get the specific heat of a material, it is not always necessary to take all of these contributions into account

**Fig. 1.1** Specific heat as a function of temperature of silicon (Si), [16] copper (Cu) and polyvinyl chloride (PVC) [17]



because, in many cases (depending on the chemical nature of the material and on temperature range), some of them can be neglected.

Specific heats of materials in the low temperature range are strong functions of temperature, as shown in Fig. 1.1; note, for example, that silicon specific heat changes by more than six orders of magnitude in the 1–200 K range.

## 1.2 Lattice Specific Heat

In this section, we will describe the lattice contribution to specific heat based on Debye's model because in many cases, it gives a reasonable agreement with experimental results. However, other models of lattice vibration of a solid have also been proposed [7, 9, 10, 12].

At high temperatures ( $T > 100$  K),  $c_V$  is essentially due to the phonon contribution  $c_{ph}$  approaching the classical Dulong and Petit value, namely,

$$c_V = 3rN_A k_B = 3rR \cong 25r \left[ \frac{\text{J}}{\text{mol K}} \right], \quad (1.6)$$

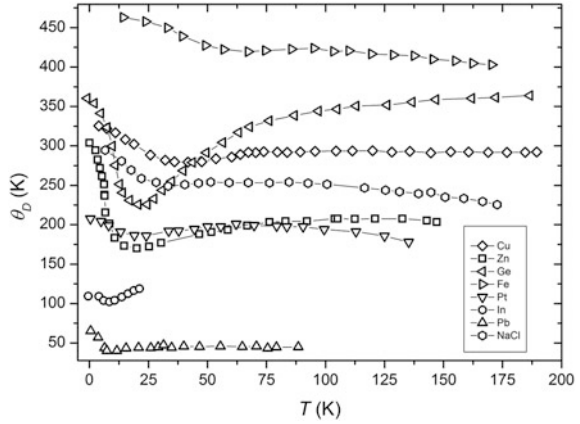
where  $r$  is the number of atoms per molecule,  $N_A$  is Avogadro's number ( $6.022 \times 10^{23} \text{ mol}^{-1}$ ),  $k_B$  is Boltzmann's constant ( $1.38 \times 10^{-23} \text{ J K}^{-1}$ ) and  $R$  is the constant of gases ( $8.31 \text{ J/mol K}$ ) [18].

For  $c_{ph}$ , Debye's elastic continuum model for solids [5–13] gives

$$c_{ph}(T) = 9rN_A k_B \left( \frac{T}{\theta_D} \right)^3 \cdot \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (1.7)$$



**Fig. 1.2** Debye temperature versus temperature for some materials. The values of Debye temperatures are obtained from heat capacity measurements [5–13]



where  $x \equiv h\omega/(2\pi k_B T)$  ( $\omega$  is the frequency,  $h$  is the Planck's constant). The integral can be solved by noting that for  $T < \theta_D$ , the upper limit of (1.7) can be extended to infinity with a small error [5, 8].

$$c_{ph}(T) = \frac{12}{5} \pi^4 r N_A k_B \left( \frac{T}{\theta_D} \right)^3 = 1944r \left( \frac{T}{\theta_D} \right)^3 \text{ [J/mol K]} \quad (1.8)$$

for temperatures  $T < \theta_D/10$ . The parameter  $\theta_D$  can be identified as the temperature above which all modes of the atoms are excited, and thus is a function of the temperature (see Fig. 1.2). In Table 1.1, we report the low temperature limit values of  $\theta_D$  for some elements.

Deviations from (1.8) depend on the chemical nature of the material as shown in Fig. 1.2. Note that for applications in thermometry, one of the requirements is that the  $\theta_D$  of the element used as a temperature sensor must remain constant in the temperature range of interest. Therefore, e.g., Platinum-based thermometers can be used in the 30–80 K range.

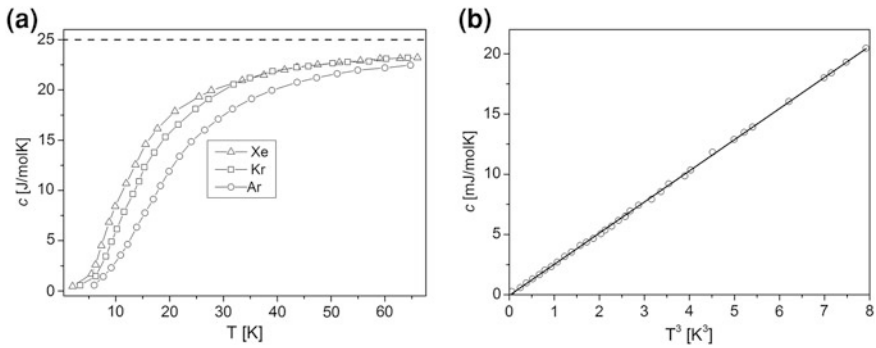
The cubic dependence of  $c_{ph}$  on temperature accounts for the small specific heat at a low temperature of crystalline insulators. The specific heat of noble gas crystals is shown in Fig. 1.3a (the dashed line represents the Dulong and Petit limit value), while Fig. 1.3b displays the  $T^3$  dependence of the specific heat of Ar below 2 K. Fitting the experimental data, it is possible to obtain  $\theta_D$  using (1.8). For example, the fit performed in Fig. 1.3b demonstrates that the measured specific heat of Ar is in good agreement with the Debye law, with a low temperature limit value of  $\theta_D$  equal to 92 K.

We wish to note that Debye theory is only applicable at low temperatures. When using (1.6) at temperature  $T > \theta_D$ , it must be recognized that the results are rough approximations.

$\theta_D$  can also be calculated by other methods [22, 23] (e.g., from the measured ultrasonic velocities) and data may be compared to those obtained from specific

**Table 1.1** Low temperature limit of Debye temperatures for some elements [10, 19]

H																	He																												
Li 344	Be 1440											B 428	C 645	N 2230	O 327	F 320	Ne 75																												
Na 158	Mg 400											Al 428	Si 645	P 374	S 282	Cl 92	Ar 92																												
K 91	Ca 230	Sc 360	Ti 420	V 380	Cr 630	Mn 410	Fe 470	Co 445	Ni 450	Cu 343	Zn 327	Ga 320	Ge 374	As 282	Se 90	Br 72	Kr 72																												
Rb 56	Sr 147	Y 280	Zr 291	Nb 275	Mo 450	Tc 410	Ru 600	Rh 480	Pd 274	Ag 225	Cd 209	In 108	Sn 200	Sb 211	Te 153	I 64	Xe 64																												
Cs 38	Ba 110	La 142	Hf 252	Ta 240	W 400	Re 430	Os 500	Ir 420	Pt 240	Au 165	Hg 72	Tl 79	Pb 105	Bi 119	Po	At	Rn 64																												
Fr	Ra	Ac																																											
<table border="1" style="width: 100%; text-align: center;"> <tr> <td>Ce</td><td>Pr</td><td>Nd</td><td>Pm</td><td>Sm</td><td>Eu</td><td>Gd</td><td>Tb</td><td>Dy</td><td>Ho</td><td>Er</td><td>Tm</td><td>Yb</td><td>Lu</td> </tr> <tr> <td></td><td></td><td></td><td></td><td></td><td></td><td>200</td><td></td><td>210</td><td>192</td><td></td><td></td><td>120</td><td>210</td> </tr> </table>																		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu							200		210	192			120	210
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																																
						200		210	192			120	210																																
<table border="1" style="width: 100%; text-align: center;"> <tr> <td>Th</td><td>Pa</td><td>U</td><td>Np</td><td>Pu</td><td>Am</td><td>Cm</td><td>Bk</td><td>Cf</td><td>Es</td><td>Fm</td><td>Md</td><td>No</td><td>Lr</td> </tr> <tr> <td>163</td><td></td><td>207</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td> </tr> </table>																		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	163		207											
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																																
163		207																																											

**Fig. 1.3** **a** Specific heat of Ar, Kr and Xe. The horizontal dashed line is the classical Dulong-Petit value [20]. **b** Specific heat of Ar as a function of  $T^3$  [10, 21]

heat measurements. The Debye's temperature evaluated from data of ultrasonic velocity can be achieved by starting from the definition of  $\theta_D$  as (see, e.g., [22, 24])

$$\theta_D = \frac{h}{k_B} \cdot \left( \frac{3N}{4\pi V} \right)^{\frac{1}{3}} v_m = \frac{h}{k_B} \cdot \left( \frac{3N_A \rho}{4\pi M_m} \right)^{\frac{1}{3}} v_m \quad (1.9)$$

where  $N$  is the number of atoms for the cell,  $M_m$  is the molar mass,  $\rho$  is the density and  $v_m$  is the mean velocity given by

$$v_m = \left( \frac{3}{1/v_L^3 + 2/v_T^3} \right)^{\frac{1}{3}} \quad (1.10)$$

where  $v_L$  and  $v_T$  are the velocities of the longitudinal and transverse waves, respectively [5]. Keeping in mind that the product  $k_B\theta_D$  indicates the minimum energy required to excite all the modes, [5] it is easy to understand that Debye's temperature is generally high for lattices made by strongly bound light atoms, as diamond ( $\theta_D = 2230$  K), and low for lattices made of weakly bound heavy atoms, as lead ( $\theta_D = 105$  K). Table 1.1 reports a lot of data referred to  $\theta_D$  of various elements; however, when two or more elements are combined to form a compound, other effects may become relevant (intermolecular weak forces, magnetic coupling etc.). Therefore, the resultant  $\theta_D$  can be difficult to predict.

### 1.3 Electronic Specific Heat

When Sommerfeld applied Fermi–Dirac statistics to free electrons in metals, it became clear why the electronic contribution to the specific heat was much smaller than the classically predicted value (1.6); in fact, by writing the internal energy in terms of density of states, we obtain

$$c_e(T) = \frac{\partial E}{\partial T} = \frac{\pi^2}{3} g(E_F) k_B^2 T \quad (1.11)$$

where  $g(E_F) = (3/2)(N_A/E_F)$  is the volumetric density of states calculated at the Fermi energy ( $E_F$ ). Substituting in (1.11) the definition of  $g(E_F)$ , [5] a linear dependence on temperature for the electronic specific heat is obtained, that is,

$$c_e(T) = \frac{\pi^2 N_A}{2 E_F} k_B^2 T = \gamma \cdot T \quad (1.12)$$

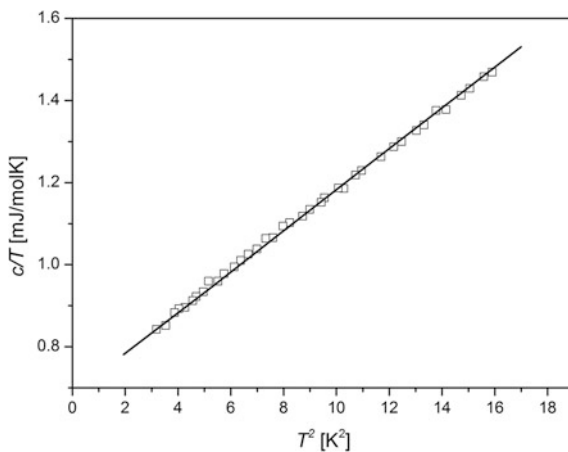
where  $\gamma$  is called the Sommerfeld constant. Knowing that  $E_F$  is of the order of some eV ( $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ ) for almost all metals, it is clear that  $\gamma$  will be of the order of  $1 \text{ mJ/mol K}^2$ . The experimental values of  $\gamma$  for some metals and alloys are reported in Table 1.2. It is worth noting that the observed values can differ from the calculated ones [10].

Thus, the total specific heat of a metal is a sum of two terms: a cubic (phononic) contribution and a linear (electronic) contribution, becoming relevant only for  $T \leq 10$  K for most materials:

**Table 1.2** Observed Sommerfeld constant of some elements in mJ/(mol K<sup>2</sup>). All data are taken from [10] except for the rare earths metals collected from [25–34]

H																	He																												
Li 1.63	Be 0.17											B 1.35	C	N	O	F	Ne																												
Na 1.38	Mg 1.3											Al	Si	P	S	Cl	Ar																												
K 2.08	Ca 2.9	Sc 10.7	Ti 3.35	V 9.26	Cr 1.40	Mn 9.20	Fe 4.98	Co 4.73	Ni 7.02	Cu 0.695	Zn 0.64	Ga 0.596	Ge	As 0.19	Se	Br	Kr																												
Rb 2.41	Sr 3.6	Y 10.2	Zr 2.80	Nb 7.79	Mo 2.0	Tc	Ru 3.3	Rh 4.9	Pd 9.42	Ag 0.646	Cd 0.688	In 1.69	Sn 1.78	Sb 0.11	Te	I	Xe																												
Cs 3.20	Ba 2.7	La 10	Hf 2.16	Ta 5.9	W 1.3	Re 2.3	Os 2.4	Ir 3.2	Pt 6.8	Au 0.729	Hg 1.79	Tl 1.47	Pb 2.98	Bi 0.008	Po	At	Rn																												
Fr	Ra	Ac																																											
<table border="1" style="width:100%; text-align:center;"> <tr> <td>Ce</td><td>Pr</td><td>Nd</td><td>Pm</td><td>Sm</td><td>Eu</td><td>Gd</td><td>Tb</td><td>Dy</td><td>Ho</td><td>Er</td><td>Tm</td><td>Yb</td><td>Lu</td> </tr> <tr> <td>10.5</td><td>24.4</td><td>22.5</td><td></td><td>12.12</td><td>5.8</td><td>10</td><td>9.05</td><td>9.5</td><td>10</td><td>13</td><td>17.94</td><td>2.90</td><td>11.27</td> </tr> </table>																		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	10.5	24.4	22.5		12.12	5.8	10	9.05	9.5	10	13	17.94	2.90	11.27
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																																
10.5	24.4	22.5		12.12	5.8	10	9.05	9.5	10	13	17.94	2.90	11.27																																
<table border="1" style="width:100%; text-align:center;"> <tr> <td>Th</td><td>Pa</td><td>U</td><td>Np</td><td>Pu</td><td>Am</td><td>Cm</td><td>Bk</td><td>Cf</td><td>Es</td><td>Fm</td><td>Md</td><td>No</td><td>Lr</td> </tr> </table>																		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr														
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																																

**Fig. 1.4** Specific heat  $c$  of copper divided by the temperature  $T$  fitted as a function of  $T^2$  [11]



$$c(T) = \gamma \cdot T + \frac{1944r}{\theta_D^3} \cdot T^3. \tag{1.13}$$

Dividing  $c$  by  $T$ , it is then possible to obtain, by a simple fit, the value of  $\gamma$ . The fit reported in Fig. 1.4 for  $c$  of copper gives  $\theta_D = 339$  K and  $\gamma = 0.684$  mJ/mol K, in good agreement with the values reported in Tables 1.1 and 1.2, respectively.

**Table 1.3** Approximate transition temperature of some elements in zero magnetic field and critical fields at  $T = 0$  K [10, 45–58]

H																	He																																																								
Li	Be															B*	C	N	O*	F	Ne																																																				
0.0004	0.026															11.2			0.6																																																						
Na	Mg															Al	Si*	P*	S*	Cl	Ar																																																				
																1.14	7	5	17																																																						
																105																																																									
K	Ca*	Sc*	Ti	V	Cr	Mn	Fe*	Co	Ni	Cu	Zn	Ga	Ge*	As*	Se*	Br*	Kr																																																								
	3	0.35	0.39 100	5.03 1420	3		2				0.875 53	1.091 51	5	0.5	7	1.5																																																									
Rb	Sr*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb*	Te*	I*	Xe																																																								
	3.5	0.006	0.546 47	9.50 1980	0.90 95	7.77 1410	0.51 70	0.0003 0.049	3.3		0.56 30	3.4035 293	3.722 309	0.35	4	1.2																																																									
Cs*	Ba*	La	Hf	Ta	W	Re	Os	Ir	Pt*	Au	Hg	Tl	Pb	Bi	Po	At	Rn																																																								
1.5	5	6.00 1100	0.12	4.483 830	0.012 1.07	1.4 198	0.655 65	0.14 19	0.0014 0.67		4.153 412	2.39 171	7.193 803	8																																																											
Fr	Ra	Ac																																																																							
<table border="1" style="width: 100%; text-align: center;"> <tr> <td>Ce</td> <td>Pr</td> <td>Nd</td> <td>Pm</td> <td>Sm</td> <td>Eu*</td> <td>Gd</td> <td>Tb</td> <td>Dy</td> <td>Ho</td> <td>Er</td> <td>Tm</td> <td>Yb</td> <td>Lu</td> </tr> <tr> <td>2</td> <td></td> <td></td> <td></td> <td></td> <td>1.8</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>0.1</td> </tr> <tr> <td>Th</td> <td>Pa</td> <td>U</td> <td>Np</td> <td>Pu</td> <td>Am</td> <td>Cm</td> <td>Bk</td> <td>Cf</td> <td>Es</td> <td>Fm</td> <td>Md</td> <td>No</td> <td>Lr</td> </tr> <tr> <td>1.368 1.62</td> <td>1.4</td> <td>2</td> <td></td> <td></td> <td>0.79</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> </tr> </table>																		Ce	Pr	Nd	Pm	Sm	Eu*	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	2					1.8								0.1	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	1.368 1.62	1.4	2			0.79								
Ce	Pr	Nd	Pm	Sm	Eu*	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																																																												
2					1.8								0.1																																																												
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																																																												
1.368 1.62	1.4	2			0.79																																																																				

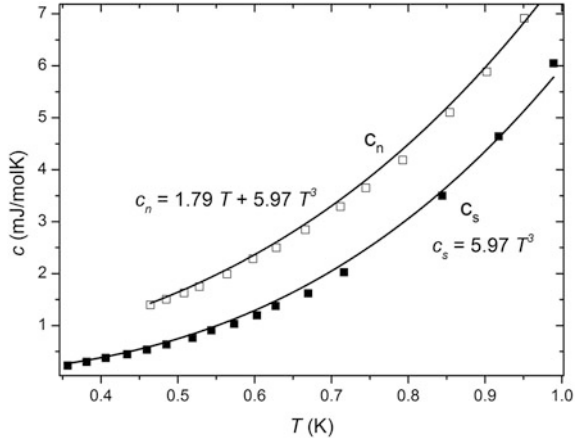
\*Superconducting only under pressure. For some elements which can assume different crystallographic structures (e.g., La, Sn), we chose one of them and invoke the appropriate references for further details. For Pt and S, the sample was a compacted powder, Pd was measured under irradiation with  $\text{He}^+$  ions and Cr was measured as a thin film

### 1.4 Electronic Specific Heat in Superconducting Materials

Materials which exhibit the phenomenon of superconductivity enter into a new state below a critical temperature,  $T_c$  (see Table 1.3). In this “superconducting state,” the electrical resistivity of the material becomes zero and its thermal properties also change.  $T_c$  is strongly affected by the applied magnetic field as well as by the purity of the material [35]. By applying a magnetic field stronger than the critical field ( $H_c$ ), the material does not enter the superconducting state as shown in Fig. 1.5, where the specific heat of Hg was measured without applied field and in a field of 1 kG [36]. We notice that the lattice specific heat  $c_{ph}$  is not modified by the superconducting transition, while the electronic contribution vanishes as temperature decreases. Using (1.8), it is possible to extract  $\theta_D = 69$  K, a value close to the one reported in Table 1.1. Calculations carried out for Hg can only be done with low  $\theta_D$  materials which present a strong phonon contribution even at low temperatures. For other materials, the behavior may be quite different if the dominant contribution to the specific heat is electronic at temperatures close to  $T_c$ .

In Fig. 1.6a, we report  $c_s$  and  $c_n$  for Al around  $T_c$  where we observe a jump,  $\Delta c_e$ , in the electronic specific heat due to the superconducting transition. For “simple” superconductors, such as Al and Sn, the Bardeen–Cooper–Schrieffer theory (BCS) [37–41] gives

**Fig. 1.5** Specific heat of Hg in the superconducting state ( $c_s$ ) and in the normal state ( $c_n$ ) [36]



$$\Delta c_e = \left. \frac{c_s - c_n}{c_n} \right|_{T_c} \cdot \gamma \cdot T_C = 1.43 \cdot \gamma \cdot T_C. \quad (1.14)$$

In Fig. 1.6a,  $\Delta c_e$  at  $T_c$  is about 2.12 mJ/mol K, giving  $\gamma = 1.30$  mJ/mol K, in good agreement with the value reported in Table 1.2. Generally, the predictions of BCS theory are in good agreement with the experimental values, except for strong-coupling superconductors as Pb or Hg [5].

Below  $T_c$ , the electronic specific heat of a superconductor,  $c_{es}$ , decreases with the temperature as (see Fig. 1.6b)

$$c_{es} = a \cdot e^{-b \frac{T_c}{T}} \quad (1.15)$$

where  $a$  and  $b$  are constants. The quantities  $a$ ,  $T_c$ ,  $\gamma$ , and  $b$  are essentially related to the zero-temperature energy gap [5]. In particular, the value of  $b$  is similar for many metals and is about 1.34 [43]. Thermodynamic arguments [44] indicate that the transition from the normal to the superconducting state at zero magnetic field does not involve a latent heat and therefore must be a higher order transition. Experimental evidence indicates that it is a second order transition.

For example, the observed specific heat of single-crystal vanadium, reported in Fig. 1.7 at  $H = 0$ , shows the form of the theoretically predicted curve. The latent heat is

$$L = T(S_n - S_s) = - \left( \frac{V H_c T}{4\pi} \right) \frac{dH_c}{dT} \quad (1.16)$$