CHAPTER 1

INTRODUCTION
1.1 HEAT CAPACITY OF SOLIDS - THEORETICAL ASPECTS AND IMPORTANCE

Heat capacity is one of the important thermal properties of the solid. An insight into the lattice dynamics can be obtained from a knowledge of the heat capacity of solids. The heat capacity $C$ of a body is defined as

$$C = \lim_{\Delta T \to 0} \left( \frac{\Delta Q}{\Delta T} \right)$$ ... 1.1.1

where $\Delta Q$ represents the amount of heat supplied to the body and $\Delta T$ represents the consequential change in the temperature rise of the body. The particular value of $C$ depends on how the thermodynamic variables of the body change during the addition of heat. Thermodynamically the most important one for the solids is the heat capacity at constant volume, $C_v$, defined by

$$C_v = \lim_{\Delta T \to 0} \left( \frac{\Delta Q}{\Delta T} \right)_v$$ ... 1.1.2

Usually the experimentally determined one is the heat capacity at constant pressure, $C_p$, defined by

$$C_p = \lim_{\Delta T \to 0} \left( \frac{\Delta Q}{\Delta T} \right)_p$$
If $U$ represents the internal energy of the system, then we can write

$$(\Delta w)_V = (\Delta U)_V$$

Hence Eqn. 1.1.2 becomes

$$C_V = \lim_{\Delta T \to 0} \frac{\Delta U}{\Delta T}_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Also we know

$$(\Delta w)_p = \Delta (U + pV)_p = (\Delta H)_p$$

where $H$ represents the enthalpy of the system. Now Eqn. 1.1.3 can be rewritten as

$$C_p = \lim_{\Delta T \to 0} \frac{\Delta H}{\Delta T}_p = \left(\frac{\partial H}{\partial T}\right)_p$$

The heat capacity of the system is also related to entropy changes given by the following equations

$$(\Delta S)_V = \int \frac{C_V}{T} \,dT$$

$$(\Delta S)_p = \int \frac{C_p}{T} \,dT$$
The above relations are valid only if there is no phase change involving latent heat in the temperature interval over which the integration is carried out.

The specific heat $C$ of a substance is usually defined as the heat capacity per gram and is given by

$$C = \frac{C}{m} \quad \text{... 1.1.10}$$

where $m$ is the mass of the sample which has heat capacity $C$. The molar heat capacity, $C_M$ is given by

$$C_M = MC \quad \text{... 1.1.11}$$

where $M$ represents the molecular weight. In the case of the elements, we have the corresponding atomic heat capacity $C_A$ defined by

$$C_A = AC \quad \text{... 1.1.12}$$

where $A$ represents the atomic weight of the element.

It is not generally feasible to maintain the solid at constant volume during temperature change and as such $C_p$ is the quantity usually measured in practice. But, $C_V$ is the quantity usually determined from theoretical calculations, and also employed in the study of lattice dynamics. These two molar heat capacities are interrelated by the following thermodynamic relation

$$C_{M_P} - C_{M_V} = \frac{V_m \alpha V^2 T}{}\beta \quad \text{... 1.1.13}$$
where \( \alpha_v \), \( V_m \) and \( \beta \) represent respectively the thermal expansion coefficient, the molar volume and the compressibility. \( T \) represents the temperature in °K at which the physical parameters involved are determined. It may be mentioned here that an exact evaluation of the difference in the heat capacities is generally not possible over a wide range of temperatures, in view of the fact that most of the determinations of \( \beta \) have been made near room temperatures. In view of this, one has to make approximations which depend on theoretical or empirical equations of state for solids. Since these approximation methods are not exact, values of \( C_v \) derived in this way are less accurate than the experimentally determined \( C_p \) data.

A commonly used approximation is based on the Mie-Grüneisen equation of state for solids, from which it follows that the Grüneisen parameter \( \gamma \) is defined by

\[
\gamma = \frac{V_m \alpha_v}{\beta C_v}
\]  

... 1.1.14

The value of \( \gamma \) ranges from 1 to 3 and is taken as independent of temperature. With this assumption, it is possible to calculate \( \gamma \) from values of \( \alpha_v \) and \( \beta \) at room temperature and then write Eqn. (1.1.13) as

\[
\left( \frac{C_p}{C_v} \right) = 1 + \gamma \alpha_v T
\]  

... 1.1.15
An empirical relation due to Nernst and Lindmann has the form \( C_p - C_v = A C_p^2 T \) where \( A \) is a constant which is evaluated by applying Eqn. (1.1.13) at a temperature \( T \) and knowing the values of \( V_m, \alpha_v \) and \( \beta \).

The high temperature heat capacity data for most of the solids have been analysed and empirically represented by the well known Dulong and Petit law. It is stated as

\[
C_v = 3Nk \quad \ldots \quad 1.1.16
\]

where \( N \) represents the Avagadro Number and \( k \) represents the Boltzmann constant. However, the experimentally observed heat capacity data below the room temperature cannot be explained based on classical theories. Quantum mechanical approach to the heat capacity of solids has been made first by Einstein\(^2\) and modified suitably to suit the data at very low temperatures by Debye\(^3\) and later developed further by Born-Vankarman\(^4\).

The experimental observations on heat capacity of solids are as follows:

For most of the solids, the heat capacity at laboratory temperature is close to \( 3Nk \). As the temperature increases above room temperature \( C_p \) and \( C_v \) increase only slightly. Below the room temperature, the heat capacity drops markedly and approaches zero as a \( T^3 \) variation in insulators.
and as $T$ in metals. Some substances such as diamond, have a value of $C_v$ at room temperature considerably less than the Dulong-Petit value.

In magnetic solids there is a large contribution to the heat capacity near the temperature at which the magnetic moments become ordered. But in the near vicinity of 0.1 K, the ordering of nuclear moments may give rise to very large heat capacities.

There are two contributions to the heat capacity of metals. One is the lattice heat capacity and the other is the electronic heat capacity. At high temperatures the lattice contribution to the heat capacity of a metal dominates over the contribution arising due to the conduction electrons. At low temperatures, the contribution to the heat capacity due to the conduction electrons dominates over the lattice contribution.

At high temperatures, the heat capacity of a metal may be expressed as

$$C_v = 3Nk + \frac{1}{2} \pi^2 N k (\frac{T}{T_F})$$

where $T_F$ represents the Fermi temperature. At temperatures much below the Debye temperature and very much below the Fermi temperature, the heat capacity of metals at constant volume may be written as the sum of electronic and lattice contributions.
The heat capacity of a material is a sensitive and revealing parameter that can detect second order transitions. It also provides important information regarding the thermodynamic stability of various phases of the material existing under different conditions. The free energy, heat content and entropy of the material can be evaluated from a knowledge of heat capacity.

\[ C_v = AT + BT^3 \]  \[ \ldots \text{1.1.17} \]

where

\[ A = \frac{\pi^2 N k}{2 T_F} \]  \[ \ldots \text{1.1.18} \]

and

\[ B = \frac{234 N k}{\Theta_D^3} \]  \[ \ldots \text{1.1.19} \]

Here \( \Theta_D \) represents the Debye temperature.

The heat capacity of a material is a sensitive and revealing parameter that can detect second order transitions. It also provides important information regarding the thermodynamic stability of various phases of the material existing under different conditions. The free energy, heat content and entropy of the material can be evaluated from a knowledge of heat capacity.
1.2 A BRIEF REVIEW OF THE EXPERIMENTAL TECHNIQUES FOR MEASUREMENT OF HEAT CAPACITIES OF SOLIDS

Most of the commonly used methods of measuring the heat capacity of solids are based directly on the defining equations. The heat content of a sample is changed by a measured amount and the corresponding change in the temperature is determined. For purposes of description, two main types of measurements may be distinguished. In one type, the Joule heat supplied as a result of current flowing in the resistance wire wound intimately around the sample, provides the change in the enthalpy and the temperature change is determined by a thermometer attached to the sample. In another type, the sample is brought to equilibrium, first with a high temperature reservoir (furnace) and subsequently with thermally isolated system, that is the calorimeter, at a lower temperature. The resulting loss in the sample enthalpy is ideally equal to that gained by calorimeter. The latter can be found from the temperature change of the calorimeter if its heat capacity is known or from the amount of calorimeter material which has undergone a phase change, if the latent heat of the phase transformation is known.

In the Nernst-Eucken method$^5$-$^7$, the heat capacity of the specimen defined by
is determined, directly by measuring the temperature increase resulting from the addition of a known quantity of heat.

In the low temperature calorimeter work, usually the method introduced by Nernst and Eucken has been employed. In this method a calorimeter containing the sample under investigation is isolated from its surroundings by means of a high vacuum and the temperature rise $\Delta T$ resulting from the introduction of a known quantity of heat $\Delta Q$ is measured. The calorimeter therefore consists of the sample and certain addenda, namely everything that is in good thermal contact with the sample during the calorimetric measurements. The primary measurements yield the heat capacity of the calorimeter, $C_{\text{cal}}$, so that it becomes necessary to determine the heat capacity of addenda ($C_{\text{add}}$) separately in order to obtain $C_{\text{sam}}$, the heat capacity of the sample.

Karasz and O'Reilly developed a wide temperature range adiabatic calorimeter which has been used for the measurement of heat capacities in the range 15–600° K. The mechanical design of the apparatus to some extent follows that of most precision low temperature calorimeters of which a typical example is that of Southard and Brickwedde.
It also incorporates some features described by West and Ginnings.\textsuperscript{10} The sample container is suspended by a ring within the principal adiabatic shield. This in turn held within a second heated shield called furnace. It is the purpose of the furnace to provide most of the heat required to maintain the adiabatic shield and sample container at any given temperature. During operation the furnace is maintained at a temperature only a few degrees below that of the shield. The differential is varied according to the absolute temperature of the system in a manner such that the power input may be kept approximately constant. Thus the thermal losses experienced by the shield are nearly independent of the temperature at which the calorimeter is operating. A further radiation shield surrounds the furnace and the entire assembly is sealed inside an evacuated chamber. The stainless steel Dewar contains either liquid nitrogen or hydrogen for low temperature operation.

Gopal Rao et al.\textsuperscript{11} developed an adiabatic calorimeter to measure the heat capacities of solids in the range 20-300\textdegree{}C. The apparatus consists of a silver calorimeter surrounded by two silver radiation shields and a brass can whose inner side is silver plated. This inner can fits into a comparatively bigger can. A vacuum of the order of $10^{-5}$ to $10^{-6}$ mm of mercury is maintained in the entire apparatus. The adiabatic conditions are observed with a differential
chromel P-alumel thermocouple which has been calibrated at selected fixed points. The performance of the apparatus has been tested by measuring the heat capacities of the standard substance α-alumina (corundum) and the values compared with those provided by National Bureau of Standards, USA. The accuracy of this technique in determining the heat capacities is ± 1.5 per cent.

Nagi Reddy designed and fabricated an adiabatic calorimeter to determine the heat capacities of some ferrite samples in the temperature range 80 K to 303 K. Though the general design of the apparatus follows the concepts of Southard and Brickwedde, the details have been differed considerably. The block method is favoured as the specimens can be ground and lapped in the form of cylindrical rods. With this calorimeter, heat capacities have been measured with an accuracy of better than 2 per cent. The measurements on heat capacities of Nickel-zinc, manganese-zinc and barium ferrites were made. It is observed that the heat capacity increases with increasing temperature in all the cases and variations are not linear in any case. Moreover, the variation of heat capacity with temperature is nearly similar to that of linear coefficient of thermal expansion in every case.
The adiabatic calorimeter developed by Antoniov and Vitvan\textsuperscript{13} is best suited for experiments of long duration such as reaction studies.

The calorimeter design differed from the conventional type in two aspects. 1. Windows have been incorporated to provide an optical path, 2. Provision had been made for easy assembly and disassembly for exchanging the specimen and adjustment of extensometer between runs. For this latter reason, the calorimeter was made of two parts and an 'O' ring was used to form the seal.

Guenter Ahlers\textsuperscript{14} developed a calorimeter to measure the heat capacities of solids between 1.3 to 20° K, with a precision of 0.1 per cent. The apparatus was very much similar to that made by Shen, Senozen and Philips\textsuperscript{15} and only special features are described. A light framework similar to the quadruped described by Martin\textsuperscript{16} was used to hold the sample. Thermal contact to the bath was made and broken with a mechanical heat switch. A manganin heater made of Formvar insulated wire and a germanium thermometer were attached to the holder. Each of the two heater current leads are attached at the isothermal shield and at the sample holder. The sample was held by three indium coated spring lead surfaces. The thermal relaxation times after heat inputs were only a few seconds. The heat capacity of the holder was measured with an accuracy of
0.2 per cent and was subtracted from total heat capacity. The heat capacity of the holder never exceeded 10 per cent of the total heat capacity.

In the drop method developed by Magnus the exchange of heat among sample (subscript s), calorimeter (subscript c) and surroundings can be expressed by the following relation

\[ H_s^1 - H_s^f = H_c^F - H_c^I + Q \quad ... \quad 1.2.2 \]

In the above equation (i) and (f) refer to initial and final states, respectively of the sample, and (I) and (F) refer to the corresponding states of the calorimeter. Q represents the heat lost to the surroundings during the course of a measurement. In the drop method, the sample is brought to its initial state by placing it along with its container in a furnace which is long compared to sample length. The larger dimensions of the furnace ensure a negligible temperature gradient in the sample. Thermocouples suitably arranged in the furnace wall adjacent to the sample are used to measure the initial temperature and to provide direct evidence of sample temperature homogeneity and equilibrium. Platinum versus platinum - rhodium or platinum-irridium thermocouples are used up to about 1200°C. The availability of suitable
thermocouples sets the upper limit of applicability of these methods. At temperatures up to several hundred °C a platinum resistance thermometer in the furnace wall may provide greater precision than thermocouples. When the sample and its container have come to equilibrium in the furnace at a temperature $T_i$, they are dropped as rapidly as possible into the calorimeter beneath the furnace.

In the method of mixtures the calorimeter consists of a container of calorimetric liquid (usually water) or a block of metal. The calorimeter is maintained at the temperature $T_i$, in isolation from a surrounding isothermal bath, prior to the sample drop. Isolation from the bath is usually achieved by using a Dewar flask to contain the calorimeter. A cover must be provided to prevent furnace radiation from reaching the calorimeter. It must be possible to remove the cover during the drop and to replace it quickly thereafter. One procedure is to use a loose fitting cover which is carried by the dropping sample into the calorimeter, while a second cover is automatically put into place by triggering mechanism actuated by the sample as it falls. A manually operated gate can also be used.

The final temperature $T_F = T_f$, is read from the calorimeter thermometer. When the calorimeter contains a liquid, stirring helps to shorten the time required to
reach the equilibrium after the sample drop. Thus, in terms of the heat capacity of the calorimeter $C_c$

$$C_s \Delta T_s = H_s(T_i) - H_s(T_f) = \int_{T_i}^{T_f} C_c \, dT + \Delta H = C_c \Delta T_c + \Delta H$$

The specific heat of the calorimeter $C_c$ may be measured directly by adding heat electrically to the calorimeter and determining the resulting temperature change. One can also evaluate $C_c$ from a knowledge of the values of the specific heats of the various calorimeter components.

Cohran et al. have developed a technique for specific heat measurements in the temperature range 1-10° K using continuous warming method. In continuous warming method, heat is added to the specimen at a constant rate $P$ and the resulting rate of increase of temperature is measured. The heat capacity is given by

$$C = \frac{P}{(dT/dt)}$$

In this method, heat is supplied to the specimen without interruption and thermometer signals are used to start or stop a clock. When the specimen temperature equals a
preset value $T_1$, the clock is started and when $T_1 + \Delta T$ is reached, the clock is stopped. The element controlled by experimenter is $\Delta T$ and the data provided by the apparatus is $\Delta T$ during the time the clock was running. Instead, in the heat burst method, the experimenter controls $\Delta T$ and measures $\Delta T$.

Chiro Hatta\textsuperscript{19} developed a method for measuring heat capacities by means of thermal relaxation method in the medium temperature range. The adiabatic methods, and the pulse or continuous warming methods require good thermal isolation of the sample. With small sample, it is hard to maintain good adiabatic conditions because the thermal leak through lead wires of the thermometer attached to the sample is not negligibly small. The thermal relaxation method makes it possible to measure the heat capacity under the existence of thermal lead rather than adiabatic conditions. A small sample is suspended by fine wires in the medium of thermal exchange gas which is surrounded by a thermal bath. The junction of the fine thermocouple wires is bonded to the sample and each wire is thermally terminated at the thermal bath. The thermocouple wires also serve to suspend the sample. If constant heat flux $Q$ is supplied to the sample by irradiation with thermal energy, the temperature of the sample increases with a relaxation time and the temperature
between the sample and the thermal bath finally reaches a saturation amplitude $\Delta T_m$. The relaxation time and saturated temperature difference are given by

$$\tau = C R \quad \ldots \quad 1.2.5$$

and

$$\Delta T_m = Q R \quad \ldots \quad 1.2.6$$

where $\tau$, $C$, $R$, and $Q$ represent the relaxation time, heat capacity, thermal resistance between sample and thermal bath and intensity of heat flux respectively.

Eliminating $R$ from Eqns. 1.2.5 and 1.2.6, we get

$$C = \frac{\tau Q}{\Delta T_m} \quad \ldots \quad 1.2.7$$

A similar method has been developed by Bachmann\(^{20}\) in the low temperature range. In this method the sample chamber is evacuated using diffusion pump. The thermal leak is provided by gold copper wires instead of thermal exchange gas. Constant heat is supplied by a heater bonded to the sample. Such a setup is found to be useful in the low temperature.

Later, Schutz\(^{21}\) has extended this method to measurements at temperatures above 35 K. It is necessary to use thicker wires as the thermal leak and as a result the sample must inevitably be larger in order to maintain high experimental precision.
1.3 AIM AND SCOPE OF THE PRESENT STUDY

Heat capacity is one of the important thermal properties of the solid. Values of the heat capacity at various temperatures can often provide information about the manner in which the internal energy is distributed among different modes of thermal excitation. Debye temperatures can be obtained by heat capacity measurements. The theory of specific heat of solids calls for an intimate knowledge of lattice vibrations of crystals and therefore of their elastic properties. Heat capacity is such a sensitive parameter that it can detect even the second order transitions. The heat capacity of the material provides important information regarding the thermodynamic stability of various phases of the material existing under different conditions. Parameters like heat content frequency, Gruneisen constant and entropy of the material can also be evaluated from a knowledge of heat capacity.

Measurement of heat capacities (specific heats) is generally limited to three temperature ranges, (i) low—below 20 K, (ii) intermediate — between 20 K and 300 K and (iii) high — above 300 K. Measurements in the intermediate temperature range can be made with a reasonably higher degree of accuracy.

In the present work, an attempt is made to design
and setup an experimental technique to determine the heat capacity of solids, like metals, alloys and polymer materials taken in the form of small cylindrical rods at room temperature (~ 30°C) with ease and higher degree of accuracy.

Development of the experimental technique forms the major part of the present programme of study. The technique is basically an adiabatic one. A calorimeter has been specially designed to suit the heat capacity measurements on small cylindrical samples of dimensions approximately 3 cm length and 6 mm in diameter. The change in the temperature of the specimen is detected using unijunction iron-constantan thermocouple and the thermo e.m.f. developed is amplified using operational amplifier network. The interval during which heat is supplied to the heater at constant current rating by Joule heating method is measured using a digital timer. The output of the operational amplifier is displayed on a digital panel meter.

Spec pure aluminium sample is used as a standard to determine the water equivalent of calorimeter and its contents. The design details of the techniques and standardization of the setup are detailed in Chapter 2. The reliability and accuracy of the technique has been tested by measuring heat capacity of standard specimens.
The heat capacity measurement technique developed in the present study has been used to study the heat capacity behaviour of multicomponent aluminium alloys with silicon as the major ingredient with a view to probe the heat capacity dependence of the alloy on the concentration of silicon and order disorder transitions if any exist. The investigations are presented in Chapter 3.
REFERENCES

1. F. Seitz
   The Modern Theory of Solids,
   McGraw-Hill, New York, 1940,
   p. 137.

2. A. Einstein
   Ann. Phys., (LPz)
   22 [1907] 180, 800.

3. P. Debye
   Ann. Phys., (LPz)

4. M. Born and
   Vankarman
   Phys. Z.,
   13 [1912] 297.

5. W. Nernst
   20 [1969] 381.

6. W. Nernst and
   A. Eucken
   36 [1911] 395.

7. W. Nernst and
   A. Eucken
   Phys. Z.,
   10 [1910] 586.

8. F. Karastz and
   J.M. O'Reilly
   Rev. Sci. Instrum.,
   37 [1966] 255.

9. J.C. Southard and
   F.G. Brickwedde
   J. Amer. Chem. Soc.,
   55 [1933] 4378.

10. E.D. West and
    Ginnings
    60 [1958] 309.

11. R.V. Gopala Rao,
    V.G. Gunjikar,
    S.G. Sankar and
    A.B. Biswas
    Ind. J. Pure Appl. Phys.,

12. B.P. Nagi Reddy
    Ph.D. Thesis,
    Sri Venkateswara University,
    Tirupati [1973].

13. A.A. Antoniov and
    G.G. Vitran
    Rev. Sci. Instr.,
    38 [1967].

14. G. Ahlers
    Rev. Sci. Instr.,
15. L.Y.N. Shen
Senozen and
Philips
Phys. Rev. Lett.,

16. D.L. Martin

17. A. Magnus
Ann. Physik,
4 [1915] 983.

18. J.F. Cohran,
C.A. Shiffmann and
J.E. Neighbour
Rev. Sci. Instr.,

19. I. Chiro Matta
Rev. Sci. Instr.,

20. R. Bachman,
F.J. Disalov, Jr.,
T.H. Geballe,
R.L. Greene,
R.E. Howard,
C.N. King,
H.C. Kirsch,
K.N. Lee,
R.E. Schwall
H.V. Thomas and
R.R. Zvbeck
Rev. Sci. Instr.,

21. R.J. Schutz
Rev. Sci. Instr.,