

3.014 MATERIALS LABORATORY

MODULE β -2

September 26 to 30, 2005

ENTHALPY OF MELTING

HEAT CAPACITY OF VARIOUS MATERIALS

OBJECTIVES

- Understand concepts of enthalpy **H**, specific heat capacity **C**, melting point **T_m**, heat of fusion **L_f**, and their relationships.
- 1). Enthalpy of Melting.
 - Perform Differential Scanning Calorimetry (**DSC**) analysis on several low melting point metals as In, Sn, Pb, and Zn.
 - Determine thermal characteristics such as **T_m**, **C_p**, and heat of fusion
- 2). Study the correlation of **C_{p,m}** with **molecular degrees of freedom**.
 - Perform DSC analysis on different crystalline non-metals such as Ge, NaCl, ZnS, FeS₂, NiS₂, CuFeS₂.

SUMMARY OF TASKS

- Prepare samples of various materials for DSC analysis.
- Obtain DSC thermograms (thermal profile) of all materials.
- Determine **molar C_p** of all materials using Al₂O₃ standard sample.
- Compare heat capacities at room temperature of various materials with similar structures to verify the effect of **molecular degrees of freedom** on **C_{p,m}**.
- Compare heat capacity values, **C_{p,m}**, at room temperature for various metals to validate the Dulong and Petit law.
- Determine **T_m**, and **heat of fusion** of low melting point metals as In, Sn, Pb, and Zn.
- Compare your data with the literature.

INTRODUCTION

- **Equipartition of Energy.**

The fundamentals of thermal properties such as heat capacity, heat content, and energy storage are related to the basic theory of equipartition of energy. How we can characterize the position of a molecule?

- For a single monoatomic molecule three coordinates must be known to fully determine the atom's position. Freedom of position is expressed by saying that a single atom has **three degrees of freedom**.
- An N-atom polyatomic molecule has 3N degrees of freedom (3N coordinates and 3 degrees for each of the N atoms).

Three types of movement can be used to describe the molecule's motion:

- Translational (motion of whole molecule).
- Rotational (rotation of whole molecule).
- Vibrational (internal vibrations within molecule).

Translation is the only type of motion for a monoatomic molecule, and can be specified as a vector sum of the motion in three directions (e.g., as three Cartesian coordinates x,y,z).

- A diatomic molecule, besides having **three** translational degrees of freedom, has, in addition, **two** rotational degrees, and **one** vibrational degree of freedom due to internal vibration, giving, in total, 6 degrees of motion (3 translational + 2 rotational + 1 vibrational = 6).
- For a linear polyatomic molecule with N atoms, there are **three** degrees of freedom due to translation and **two** due to rotation.
- The motion of a nonlinear polyatomic molecule can be specified by three translational degrees of freedom, three rotational degrees, and (3N-6) degrees for vibrational motion.

Translational energies are **quantized**, but their spacing is too small and a virtual continuum of energy levels can be considered.

Rotational motion requires more energy than translation to be excited, which is reflected in a wider spacing of rotational energy levels relative to translational energy levels.

It takes much more energy for a vibrational motion to be excited, and its energy levels are higher relative to rotational energy levels.

The principle of equipartition states that **the contribution of each type of energy to the internal energy, U, is equal to $1/2kT$** (where k is Boltzmann's constant and T is absolute temperature) **per degree of freedom** [1,2].

Translation and rotation can be characterized only by kinetic energies, but vibration, in addition, possesses potential energy, thus each vibrational degree of freedom contributes $2 \times 1/2kT$ to the internal energy. This simple theory of equipartition allows us to evaluate the contributions of degrees of freedom to U, and hence to the heat capacity.

Example:

There are only three degrees of freedom for a monoatomic gas (all belong to translation). Thus, $U=3 \times 1/2kT$, which is the same result found from the kinetic theory of gases.

● **Heat Capacity of Solids.**

In 1819 Dulong and Petit experimentally found that for many solids at room temperature $C_{p,m}$ is nearly $3R=25J/Kmol$. The Dulong and Petit law can be explain based on equipartition theory. For each atom in a monoatomic solid there are 3 degrees of freedom. Each of those three degrees can be expressed in terms of vibrational motion of the atoms at sites of the lattice.

Based on equipartition theory, this gives, per atom

$$U = 3 \times 2 \times 1/2kT = 3kT$$

and

$$C_v = 3k$$

Considering that for solids $C_p \approx C_v$ it results on a molar basis that

$$C_{p,m} \approx 3R$$

● **Effect of Molecular Degrees of Freedom on Heat Capacity.**

The molar heat capacity at constant pressure $C_{p,m}$ measures the heat capacity of a material having a fixed number of particles N_A (Avogadro's number).

The heat capacity of all materials tends to zero as temperature T approaches zero. $C_{p,m}$ increases quickly in the 25-100K temperature range, then bends and begins to saturate near room temperature. Not all crystals have values of $C_{p,m}$ whose rapid increase plateaus near room temperature [1,3]. The characteristic temperature above which $C_{p,m}$ is close to $3R$ and

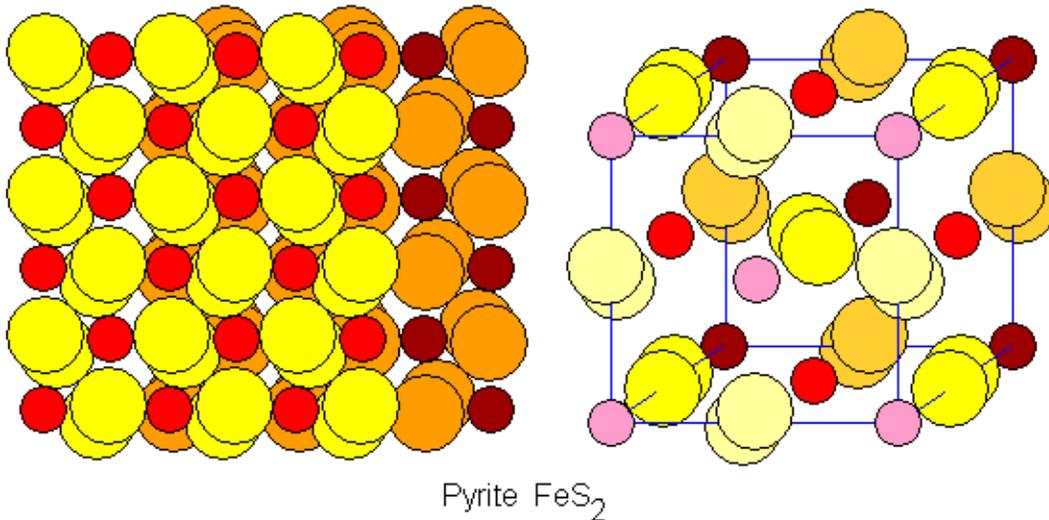
below $C_{p,m}$ increases quickly with T , is called the *Debye* temperature, and depends on material properties.

In order to understand the effect of molar degrees of freedom on $C_{p,m}$, we will focus in several crystalline non-metals which exhibit similar inner structures.

In the Ge, Zn, Pb, and Sn, single atoms are located at lattice sites and therefore one mole of these crystals contains N_A vibrating particles. For this reason the value of $C_{p,m}$ at room temperature is close to $3R$ where $R=k N_A$ is the Universal gas constant.

- For halite structures such as NaCl, atoms of Cl arrange in a face centered cubic structure, with Na atoms occupying the octahedral sites; thus one mole of NaCl consists of N_A sodium atoms and N_A chlorine atoms, giving in total $2N_A$ particles. The value of $C_{p,m}$ therefore plateaus to $6R$.

- **Pyrite Structure.** For NiS_2 (nickel sulfide), FeS_2 , $FeSe_2$, and $NiSe_2$, called **pyrite** structures, two types of atoms are located in lattice sites forming a modified halite structure, as is shown in Fig.1,a. [ref. www.uwgb.edu/dutchs/PETROLOGY/PyriteStructure.htm].



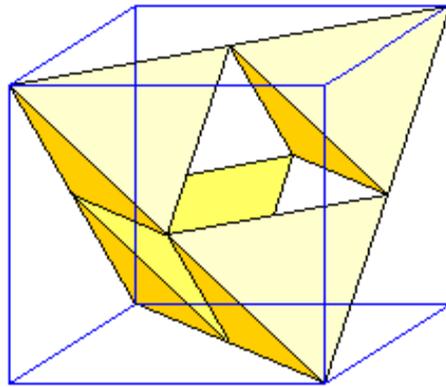
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Fig.1

The transition-metal disulfides MS_2 ($M=Mn, Fe, Ni, Co, Zn$) crystallize in the cubic pyrite structure which can be considered as a NaCl-like grouping of metal atoms and atomic pairs of S_2 . The atoms of the S_2 are linked by a strong covalent bond. In contrast, the metal –sulfur bond is essentially ionic.

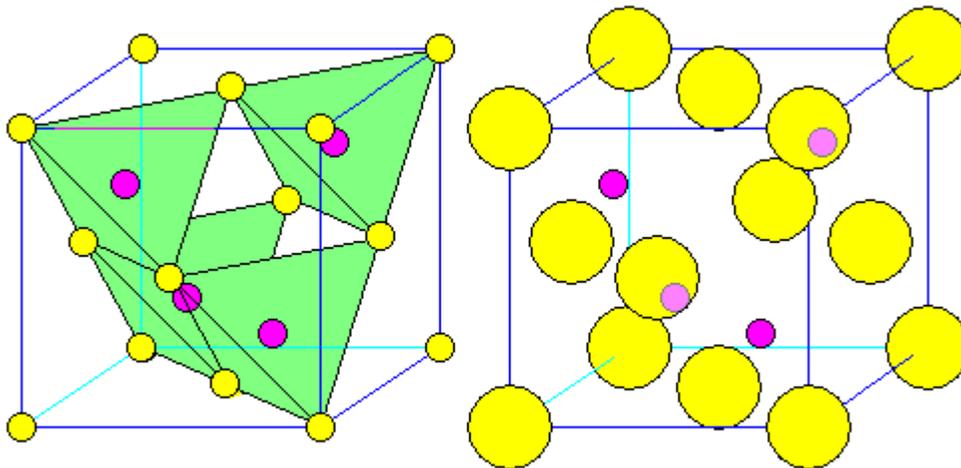
There are $3NA$ particles vibrating at their lattice sites, and one can expect a $C_{p,m}$ value nearly equal to $9R$ at room temperature for pyrite structures.

- **Sphalerite (ZnS)** is one of a number of minerals whose structure is based on inscribing tetrahedra in a face-centered cubic structure, as is shown in Fig.2 [ref.www.uwgb.edu/dutchs/PETROLOGY/Sphal-ChalcStructure.htm]. Sphalerite structure is a face centered cubic arrangement of sulfur atoms (yellow) located in cube corners and zinc atoms in the center of half the tetrahedral sites (purple), as is shown in Fig.2,b. At left is the structure illustrating the occupied tetrahedra, and at right is the unit cell.



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Fig. 2, a



Sphalerite ZnS

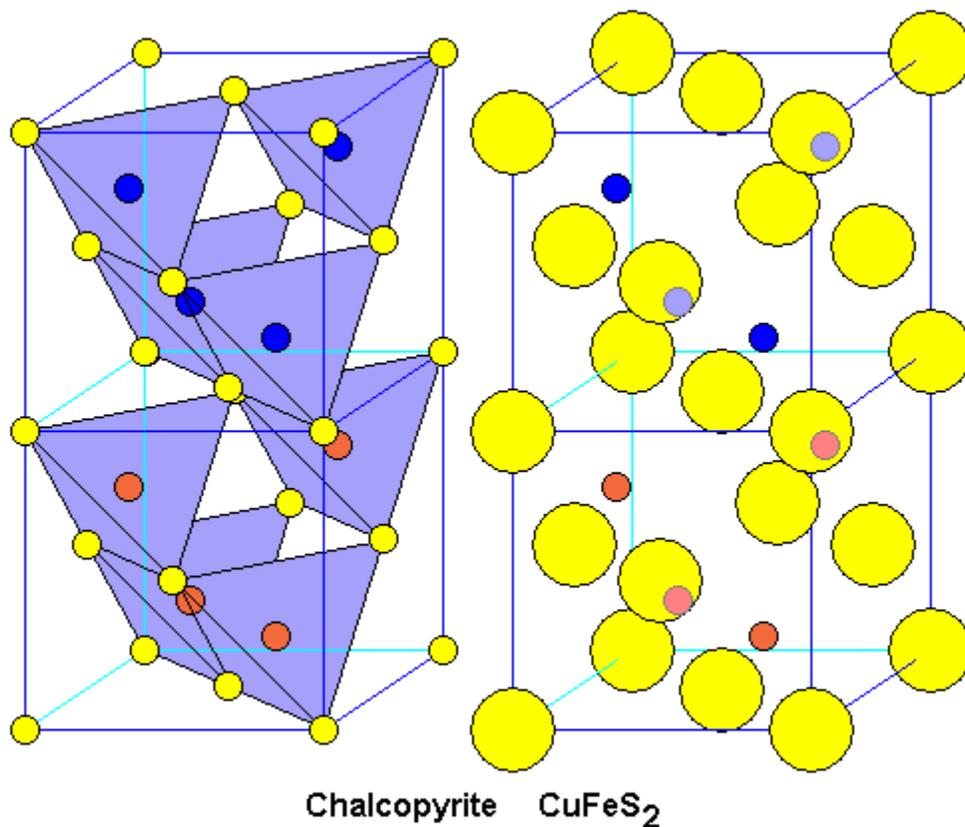
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Fig.2, b

- **Chalcopyrite (CuFeS₂)**

Chalcopyrite has a very similar structure to sphalerite, as is shown in Fig.3. [ref. www.uwgb.edu/dutchs/PETROLOGY/Sphal-ChalcStructure.htm].

Cells with Fe atoms (orange) alternate with cells containing Cu atoms (blue). S atoms are located in cube corners. This double cell means chalcopyrite is tetragonal. **What value of C_{p,m} would be expected for this structure at room temperature?**



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Fig. 3

EXPERIMENTAL

- **MATERIALS**

- Several low melting point metals such as In, Sn, Pb, and Zn, as well as non-metal crystals such as NaCl, ZnS, NiS₂, FeS₂, CuFeS₂ are studied in this Module.

In order to reveal thermal properties T_m , $C_{p,m}$, heat of fusion, as well as to demonstrate the effect of molecular degrees of freedom on molar heat capacity at constant pressure, validation of the Dulong and Petit law, a DSC technique is employed.

● **METHOD**

DIFFERENTIAL SCANNING CALORIMETRY [DSC] – TA INSTRUMENTS – MODEL Q100

DSC- Analysis (adapted from 3.014 Module Beta-1 Notes)

INTRODUCTION

DSC is a thermal analysis technique useful for measuring thermal and thermodynamic properties of materials such as the specific heat, melting and boiling points, glass transitions in amorphous/semi-crystalline materials, heats of fusion, reaction kinetics etc. The technique measures the temperature and the heat flow (in desired units, mW, W/g etc.) corresponding to the thermal performance of materials, both as a function of time, and temperature.

The TA Instruments DSC is a “HEAT FLUX” type system where the differential heat flux between a reference (e.g., sealed empty Aluminum pan) and a sample (encapsulated in a similar pan) is measured. The reference and the sample pans are placed on separate, but identical stages on a thermoelectric sensor platform surrounded by a furnace. As the temperature of the furnace is changed (usually by heating at a linear rate), heat is transferred to the sample and reference through the thermoelectric platform. The heat flow difference between the sample and the reference is then measured by measuring the temperature difference between them using thermocouples attached to the respective stages.

The DSC provides qualitative and quantitative information on endothermic / heat absorption (e.g., melting) and exothermic / heat releasing (e.g., solidification or fusion) processes of materials. These processes display sharp deviation from the steady state thermal profile, and exhibit peaks and valleys in a DSC thermogram (Heat flow vs. Temperature profile). The latent heat of melting or fusion can then be obtained from the area enclosed within the peak or valley.

Some factors that may affect the DSC measurements are :

- Sample positioning on the DSC stage (variations in baseline)
- Structure and mass of the sample (proper thermal contact)

- Heating rate (Trade-off between sample attaining thermal equilibrium and data acquisition times. A fast heating rate may minimize the data acquisition time compromising salient features of the material properties)

Note:

1. Due to time constraints, deviation from controlled procedure is to be expected;
2. It may not be possible to measure the properties of the material prepared during the lab session. You may be provided with samples that are already prepared as above.

● **SAMPLE PREPARATION FOR (DSC) MEASUREMENTS.**

Weigh 5-20 mg of the material and spread it uniformly in a NORMAL aluminum pan to ensure proper thermal contact. Crimp the pan with the lid.

● **EXPERIMENTAL PROCEDURE.**

1. Obtain a **baseline (zero line)** thermal profile (Heat Flow vs. Temperature with empty, identical (equal mass) aluminum pans placed on the reference and the sample stages, respectively.

The aluminum pan on the reference pan must be crimped.

The pan on the sample stage is left uncrimped for later use.

The baseline scan corrects for any asymmetry of the system.

SCAN conditions:

- Set point temperature: 15°C.
- **Mass of the sample:** enter the weighed amount for each sample in mg (5.00 – 20.00 mg)
Input, 0 (ZERO) for the mass of the empty pan in baseline scan
- Scan Mode: **RAMP**
- **Heating rate:** @ 10° C / min scan from 15 to 400° C

Ideally, an independent baseline profile must be obtained for each sample using the same pan in which it will be placed. However, in the present study, only one baseline scan will be performed for all samples, assuming identical mass or volume for all the pans (select pans and lids of similar masses).

Leave the pan on the reference stage undisturbed for the remaining measurements.

2. Obtain a thermal profile with a calibration standard (e.g. Sapphire) using the same scan conditions as in Step 1.

This provides a calibration factor that translates the measured Heat Flow units (in mW) to Heat Capacity units (J/g°C).

Place the crimped pan containing the calibration standard (sapphire, mass = 25.68 mg) on the sample stage.

3. Obtain thermal profiles for all samples using same scan conditions as in Steps 1 and 2.

Place each crimped pan containing the weighed amounts of sample on the sample stage.

4. Subtract the baseline data from the sample and the sapphire data, prior to analysis.

5. Analyze the data as explained below. [Bring zip disk to store data files]

● **DATA ANALYSIS.**

SPECIFIC HEAT Calculation

[see hand out: Quantitative Analysis – TA Instruments]

1. Calculate the specific heat (C_p) of each sample @ 25 ° C (solid phase)

$$C_p = \frac{C_p(\text{sapphire}) \times m(\text{sapphire}) \times \Delta H(\text{sample})}{\Delta H(\text{sapphire}) \times m(\text{sample})}$$

where,

ΔH is the heat flow (in mW) at a given temperature, obtained from the baseline subtracted plot of Heat Flow (mW) vs. Temperature for each sample, and for the sapphire standard; m is the mass of each sample, and sapphire (in mg).

Note:

- The table in the hand-out provides the C_p (sapphire) values as a function of temperature. Extrapolate if necessary.
- The known C_p (sapphire) values at a given temperature, translates the measured Heat Flow (in units of mW) to Heat Capacity units (J/g °C).
- The above equation is obtained by writing the equation for C_p explicitly for the sample and for sapphire, and dividing the two equations [4,5].

- **MELTING POINT and LATENT HEAT OF FUSION**

1. Use the **Universal Analysis** software of the DSC and the peak integration routine to determine from the thermal profile, the latent heat of melting, and the melting temperature for each sample.

REFERENCES:

[1] Lecture Notes of 3.012 course

[2] M.A. White “Properties of Materials” Oxford university Press, 1999, Ch. 6.

[3] Zemansky, M.W. and Dittman, R.H.,”Heat and Thermodynamics”, McGraw-Hill, New York, 1997, pp.233-236.

[4]. “Guidelines for Quantitative Studies – Heat Capacity Experiments”
TA Instruments Manual DSC 2920, 4-15 – [HANDOUT]

[5] D3947- 80. Annual Book of ASTM Standards, Part 25, ASTM, Philadelphia, PA
(1980)

