Specific heat and Debye Temperature of Zinc Sulphide

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ABSTRACT:

The specific heats of ZnS at different temperatures have been computed based on the force model developed in the present work. According to this theory, the specific heat of a gram-atom of any solid at any temperature is shown to be equal to 3Nk, where k is the Boltzmann's constant and N is Avogadro's number. A brief account of different theoretical approaches to explain the specific heat of solids is given in this work. These theories have been developed to explain the available experimental results of specific heats of solids.

KEYWORDS: FORCE FIELD MODEL, BOLTZMANN CONSTANT, AVOGADRO'S NUMBER

INTRODUCTION:

Zinc Sulphide is the most extensively studied compound as regards the lattice dynamical and thermodynamical properties Clausius and Harteck [6] reported the experimental values of the specific heats and Debye temperatures of zinc sulphide. Experimental investigation of the thermodynamic properties of this crystal has been also made by Martin[2]. The measurements of Martin were limited to lower temperatures. The work on the experimental determinations of specific heats and Debye temperatures for ZnS is due to Birch et al[4] and Vekilov and Rusakov[11].

Theoretical investigations of the thermodynamic properties of zinc sulphide with the application of lattice dynamical models have been made by Blackman[7], Banerjee and Varshani[9], Vetelino and Mitra[5] and Vegelatos et al[8]. Vetelino and Mitra[5] presented the theoretical results for the calorimetric Debye temperatures of this compound on the basis of the rigid ion model which is essentially the model used by Rajagopal and Srinivasan[1]. Debye temperatures of the zinc sulphide crystal have been reported by Wooster[10]

METHODOLOGY

The force field model has been developed for describing the specific heat and Debye Characteristic temperature of ZnS. This theoretical model is based on vibrations and frequency of the atom.

From Dulong–Petit law, the atomic heat at constant volume can be obtained from the relation

$$C_P - C_V = \beta^2 KVT \qquad 1$$

Where C_P and C_V stand for the atomic heats at constant pressure and constant volume respectively; β is the temperature coefficient of volume expansion at constant pressure, K is the isothermal bulk modulus, and V and T are the atomic volume and absolute temperature respectively. A theoretical explanation of the Dulong-Petit law was first given by Richarz[3] based on the kinetic theory of matter. According to him, the atomic specific heat at constant volume was found to be, as stated earlier, equal to 3R which comes out to be 5.96 cal./deg.-at.wt. According to the kinetic theory, the specific heat is found to be independent of temperature

EINSTEIN'S THEORY OF SPECIFIC HEAT

The model of solid adopted by Einstein consisted of atoms, each of which vibrates with the same frequency . The vibrations were assumed to be governed by the quantum hypothesis. According to Einstein, the mean energy of an oscillator is given by

$$\varepsilon = \left(\frac{h\nu}{e^{-h\nu/kT}-1}\right) \qquad 2$$

The total energy of a gram atom of a monoatomic solid is given by

$$E = \frac{3Nh\nu}{\left(e^{h\nu/kT}-1\right)} \qquad 3$$

where N is the number of oscillators in a gram atom of the solid.

The atomic heat at constant volume is thus given by

$$C_V = 3R(kTh\nu)2\left(\frac{}{e^{h\nu/kT}-1)2}\right. \qquad 4$$

The result of Einstein's theory of specific heat predicted that the value of C_V tends to zero as the value of T tends to zero. However, the experimental data of specific heat at very low temperatures are only in qualitative agreement with Einstein formula. Einstein[7] himself concluded that the disagreement of his theory with experiment at low temperatures was due to the assumption of a single frequency.

DEBYE'S THEORY OF SPECIFIC HEAT

In Debye's theory of specific heat of solids, the single Einstein frequency is replaced by a frequency spectrum

The number of standing sound waves present in the solid with frequencies between and +d is assumed to determine the spectrum

The energy of the system according to Debye's theory is

$$E = \sum_i n_i h\nu/(e^{h\nu/kT}-1) \qquad 5$$

Where $3N = \sum_i n_i$

The Debye's characteristic temperature θ_D is introduced through the relation

$$k\theta_D = h\nu_D \qquad 6$$

The equation for the energy of a gram-atom of a solid is transformed to the following form

$$E = 9RT^4/\theta_D^3 \int_0^{\theta_D} \frac{\phi^3 d\phi}{e^{\phi}-1} \qquad 7$$

where $\boldsymbol{\varphi = \frac{kT}{h\nu}}$ and $\boldsymbol{d\varphi = \frac{h}{kT}d\nu}$

The general expression for the atomic heat of Debye-model solid is

$$C_V = 3R\left|12(T/\theta_D)^3 \int_{0_{D/T}}^{0} \frac{}{\phi\phi d-\phi 1} - 3T\theta_D/(\varepsilon\phi-1)\right] \qquad 8$$

The term in the rectangular bracket is a function of □ and is known as Debye function

$$_{D}(\phi) = 12(T/\theta_D)^3 \int_0^{\theta_D/T} \frac{\phi d\phi}{(e^{\phi}-1)} - \frac{3\theta_D}{T}/(\varepsilon^{\phi}-1) \qquad 9$$

EVALUATION OF SPECIFIC HEAT AND DEBYE TEMPERATURE

The evaluation of the specific heat is possible, as it is evident from the preceding discussion, only when the vibrational frequencies in the lattice are completely determined. The expression for the gramatomic specific heat at constant volume is

$$C_V = 3NR\sum_{\nu} g(\nu)E(\nu) \qquad 10$$

where

N = 1/3 mn m = number of divisions in the first Brillouin zone n = number of atoms in unit cell R = Universal gas constant $g(\nu)d\nu$ is the number of modes with frequencies lying between □ and □+**d**□. g(ν)is called the frequency distribution function for the solids. **E (□)** is called the Einstein function defined by

$$E(\nu) = (\_\_\_\_\_ \exp h\nu)^2 (h\exp_{\nu}/kT(h\nu-/1kT)_2) \qquad 11$$

In case of zinc blende crystals, there are two atoms per unit cell and hence the expression (10) for the specific heat reduces to

$$C_V = 3R/6000\sum_{\nu} g(\nu)E(\nu) \qquad 12$$

RESULTS AND DISCUSSIONS

As there is variation of specific heat with temperature, the specific heats for these compounds which are obviously of zinc blende structure have been calculated at different temperatures. The specific heat versus temperature curve is rather than insensitive test of the force model used for the lattice vibrations of solids. In fact, even with the simple models of Debye and Einstein, one may obtain reasonably good agreement of specific heat versus temperature data with experiment. In order to obtain a more sensitive test of the specific heat and hence the force model one resorts to the use of the Debye temperature given by the equation

$$\theta_D = h\nu_D/k$$

The specific heats of ZnS at different temperatures have been computed on the basis of the force model developed in the present work. The results are found to be in good agreement with the calculated and the experimental observations (Fig.1).

Calorimetric Debye temperatures have been also calculated at various temperatures. The calculated results of calorimetric Debye temperatures agree satisfactorily with the experimental data (Fig.2).

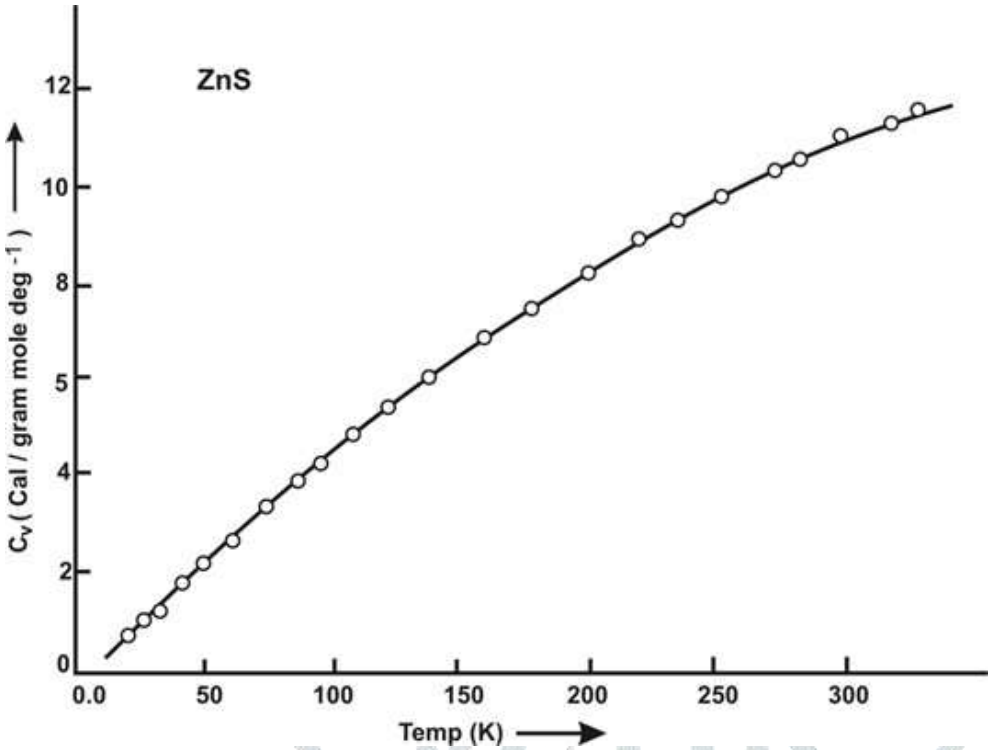

Fig.1 : CV versus temperature curve for zinc sulphide. Circles are experimental results (Ref. 13)

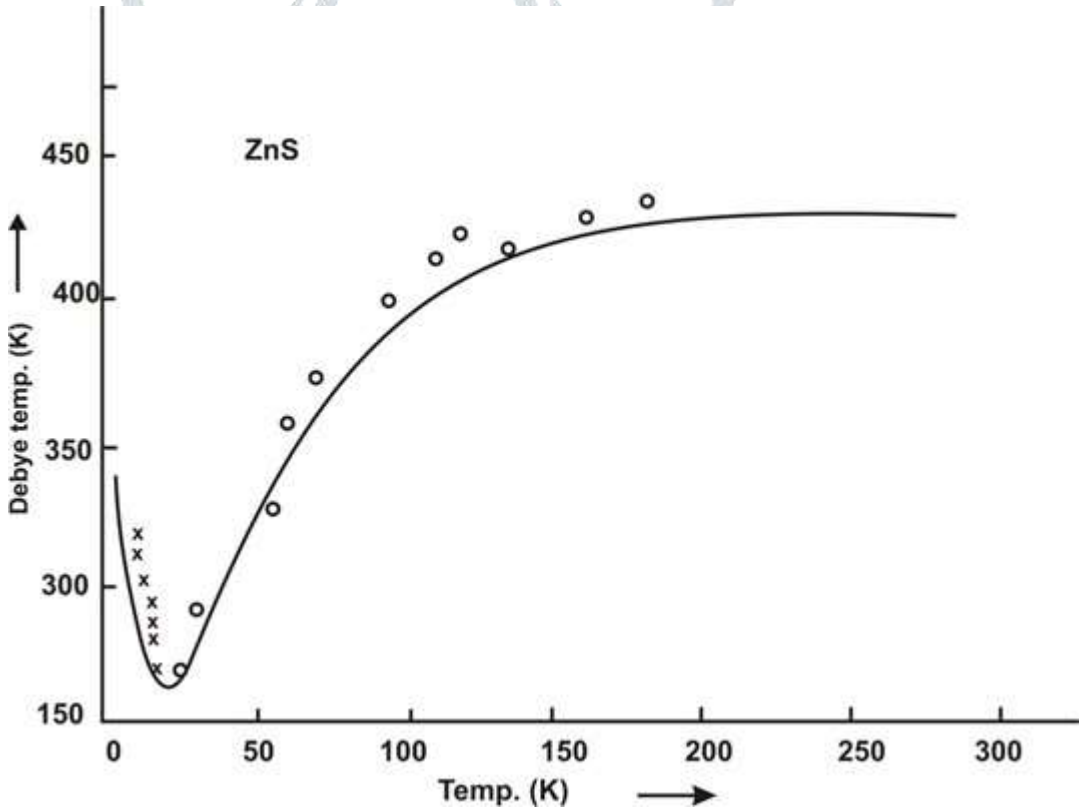

Fig. 2 : θ_D versus temperature curve for zinc sulphide. Circles and crosses are experimental results

CONCLUSION

Results for specific heats and Debye temperatures of several binary compounds crystallizing in zinc blende structure have been obtained on the basis of a theoretical lattice dynamical model developed in the present work

Thus, the present model explains satisfactorily the experimental and other theoretical results for zinc blende and diamond structure crystals

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