X-Ray Debye temperature study of Gruneisen constant of Hexagonal Phase Cu$_{1-x}$Zn$_x$ alloys

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Abstract. Hexagonal Close Packed (HCP) phase Copper-zinc (Cu$_{1-x}$ Zn$_x$) alloys have been discussed with compositions (x = 79.20, 82.00, 84.30, 86.10, 97.10, 97.50, 98.10, 98.60, 99.50). These alloys have been prepared from spectroscopically pure copper (Cu) and zinc (Zn) metals by melting using the glass blowing and vacuum sealing process with appropriate quantities in evacuated quartz tubes. For the duration of melting process the alloy/mixture was systematically stirred for homogenization. The powder samples of all the Cu$_{1-x}$ Zn$_x$ alloys were prepared by gently filing the ingots with jeweller’s file. The evaluated Debye temperature values were compared with Debye temperature values evaluated from Kopp-Neumann relation and other four relations composition dependence relation, specific heat relation, empirical relation, Gril and Mittra relation. Gruneisen constant of hcp phase Cu$_{1-x}$Zn$_x$ alloys were evaluated utilizing a relation associated with Debye temperature values were measured from X-Ray diffraction method.

1. Introduction
Gruneisen constants is an important solid state parameter. It has considerable theoretical and experimental work on the determination of Debye temperatures of some hcp Cu$_{1-x}$Zn$_x$ alloys. Influence of Tool Revolving on Mechanical Properties of some metals and alloy had been developed as next generation engineering production [1,2] and with some thermal and mechanical properties and engineering applications [3,4]. Bansigir [5] had shown that log $\rho$-log V plot for a family of crystals is linear and its slope represents the mean Gruneisen constant for the family of crystals. He applied this concept to data for metals and alkali halides with NaCl structure and obtained reasonable values for the Gruneisen constant. The composition dependence of the Debye temperature of alloys have been studied by earlier workers [6-7]. But such studies on the hexagonal alloys are scanty. In the present investigation the results of a systematic study hcp phase Cu$_{1-x}$Zn$_x$ alloys are reported first time.

2. Experimental
Hexagonal Close Packed (HCP) phase Copper-zinc (Cu$_{1-x}$ Zn$_x$) alloys have been discussed with compositions (x = 79.20, 82.00, 84.30, 86.10, 97.10, 97.50, 98.10, 98.60, 99.50). These alloys have been prepared from spectroscopically pure copper (Cu) and zinc (Zn) metals by melting using the glass blowing and vacuum sealing process with appropriate quantities in evacuated quartz tubes. For the duration of melting process the alloy/mixture was systematically stirred for homogenization. The final different compositions have been arrived at after subjecting these Cu$_{1-x}$ Zn$_x$ alloys to spectroscopic
analysis. The powder samples of all the Cu$_{1-x}$Zn$_x$ alloys have been prepared by gently filing the ingots with jeweller’s file. X-ray measurements have been taken by X-Ray diffractometer. (Philips 3020, fitted a proportional counter with CuK$_\alpha$ radiation. The X-ray diffraction patterns of hcp Cu$_{1-x}$Zn$_x$ alloys are shown in Figure 1 (a-i). Chipman and his co scholar [8] has been discussed integrated intensities.

3 Characterization Techniques

3.1 Debye Temperature

Cu$_{1-x}$Zn$_x$ alloys with different compositions belong to hcp structure. The integrated intensity [9-11] is written by

\[ I_0 = C I \exp \{-(4\pi \sin \theta / \lambda)^2 [<u_c^2> \cos^2 \psi + <u_a^2> \sin^2 \psi] \} \]

The intensity value \( I \) is

\[ I = I_0 |F|^2 , \]

The structure factors for fcc lattice is given by

\[ F^2 = 16f^2 \] for \( h,k,l \) are all even

\[ F^2 = 16f^2 \] for \( h,k,l \) are all odd

\[ F^2 = 0 \] for \( h,k,l \) mixed

For the hexagonal close-packed structure, \( F \) values are given by

\[ F_{hkl}^2 = 4f^2 \] for \( h + 2k = 3n \), \( l = \text{even} \)

\[ F_{hkl}^2 = 3f^2 \] for \( h + 2k = 3n \pm 1 \), \( l = \text{odd} \)

\[ F_{hkl}^2 = f^2 \] for \( h + 2k = 3n \pm 1 \), \( l = \text{even} \)

For the Cu$_{1-x}$Zn$_x$ alloy, the atomic scattering factor \( f \) is written as

\[ <f> = X_{Cu} f_{Cu} + X_{Zn} f_{Zn} \]

Where \( X_{Cu} \), \( X_{Zn} \) and \( f_{Cu} \), \( f_{Zn} \) are the atomic concentrations and atomic scattering factors of Cu and Zn respectively.

The structure factors (\( F \)) were clearly discused by Cromer and Waber [12]. The values have been corrected from anomalous dispersion [13]. \( <u_c^2> \) values and \( <u_a^2> \) values have been measured from a least squares analysis of the logarithmic form the equation 1. The directional Debye-Waller factors \( B_a \) values and \( B_c \) values have been measured from the following equations

\[ B_a = 8\pi^2<u_a^2>, \quad B_c = 8\pi^2<u_c^2> \]

The average or mean Debye-Waller factor \( B \) is

\[ B_{ave} = (2B_a + B_c)/3 \]
Figure 1(a)–(i). The XRD patterns of Cu_{1-x}Zn_{x} alloys.

Directional Debye temperatures $\theta_a$, $\theta_c$ values and mean Debye temperature $\theta_M$ values have been evaluated from $B_a$ values, $B_c$ values and $B_{ave}$ values respectively by utilizing the Debye-Waller theory [11] relation,

$$\overline{B} = \left( \frac{6h^2}{M k_B \theta_M} \right) W(X)$$
\[ B_a = \left( \frac{6h^2}{M k_B \theta_a} \right) W(X) \]
\[ B_c = \left( \frac{6h^2}{M k_B \theta_c} \right) W(X) \]

Where, \( h \) is the Planck’s constant, \( k_B \) the Boltzmann constant

The function \( W(X) \) is given by
\[ W(X) = \left[ \frac{\phi(X)}{X} + (1/4) \right] \]

Where, \( X = \theta_M / T \), \( \phi(X) \) is the Debye function. \( W(X) \) values and \( X \) can be evaluated from the standard tables [14]. The data on Cu and Zn has been processed by assuming isotropic amplitude of vibration.

### 3.2 Gruneisen constant from Debye Temperatures

In terms of experimentally observed quantities, the Gruneisen parameter is given by
\[ \gamma = \left( \frac{\beta V}{\psi C_v} \right) \]

where \( \beta \) is the coefficient of volume expansion, \( V \) the atomic volume, \( \psi \) the compressibility and \( C_v \) the molar specific heat. These values of \( \gamma \) refer to as \( \gamma \)-thermal.

The comparison of the values of Gruneisen parameter is made in the light of the following points; (i) strictly speaking, each crystal will have its own Gruneisen constant and this method assumes a common Gruneisen constant for the entire solid solution system. (ii) it is an approximate method. By definition
\[ \gamma = \frac{-d\log \theta}{d\log V} \]

In the current work, the log\( \theta \)-log\( V \) plots for hexagonal phase of Cu\( _{1-x} \)-Zn\( _x \) alloys are calculated.

### 4 Results and Discussion

X-ray Debye temperature \( \theta_M \) values of the hexagonal phases Cu\( _{1-x} \)-Zn\( _x \) alloys are given in the Table 1. The Debye temperature (experimental) values were plotted as the function of composition in the Figure 2 for hexagonal phase. For the Cu\( _{1-x} \)-Zn\( _x \) alloys system the composition dependence of the Debye-temperature show a slight positive deviations from linearity for both the phases.

Several relations are available in literature which represents the composition dependence of the Debye temperature of alloys. One such relation is the Kopp-Neumann relation,
\[ \theta_c^{-3} = x \theta_A^{-3} + (1-x) \theta_B^{-3} \]

Where, \( x \) is the composition and \( \theta_c, \theta_A \) and \( \theta_B \) are the Debye temperature of the alloy and the pure constituents. There are other relations available in literature for the description of composition dependence of Debye temperature of alloys.

| Composition   | \( \theta_M \) (K) |
|---------------|-------------------|
| Cu\(_{20.86}\)Zn\(_{79.20}\) | 238(9)            |
| Cu\(_{18.06}\)Zn\(_{82.00}\) | 237(6)            |
| Cu\(_{15.76}\)Zn\(_{84.24}\) | 234(7)            |
| Cu\(_{13.96}\)Zn\(_{86.10}\) | 232(7)            |
| Cu\(_{2.90}\)Zn\(_{97.10}\) | 228(6)            |
Cu_{2.50}Zn_{97.50} \quad \theta_M = 221(6) \\
Cu_{1.90}Zn_{98.10} \quad \theta_M = 220(6) \\
Cu_{1.40}Zn_{98.60} \quad \theta_M = 219(8) \\
Cu_{0.50}Zn_{99.50} \quad \theta_M = 216(3)

Figure 2. Plot of Debye temperature ($\theta_M$) vs composition (x)

\[ \theta_c^2 - \theta_A^2 + (1-x) \theta_B^2 = x \theta_A^2 + (1-x) \theta_B^2 \]

Nagaiah and Sirdeshmukh (4) combined the high temperature approximation for the specific heat from Debye’s theory and the additivity of specific heats and obtained the relation

Further, they also proposed the empirical relation

\[ \theta_c^{-1} = x \theta_A^{-1} + (1-x) \theta_B^{-1} \]

Giri and Mitra (5) proposed the relation

\[ m_{AB} \theta_{AB} = x m_A \theta_A^2 + (1-x) m_B \theta_B^2 \]

All these equations were critically examined by Geeta Krishna by applying the data on seven mixed crystal systems with NaCl structure and comparing the calculated values with the experimental values. From the comparative study, Geeta Krishna et al concluded that the Kopp-Neumann relation provides the best description for the composition dependence of Debye temperatures of the mixed crystal systems with NaCl structure. Balaiah (2003) made a critical examination of these equations by applying the data on mixed crystal systems with CsCl structure and arrived at the same conclusion.

Such a critical examination has now been undertaken for Cu_{1-x}Zn_{x} alloys. Hence, it is proposed to compare the experimental data obtained for the Cu_{1-x}Zn_{x} alloy system in the present investigation and the data evaluated from the equations from 12 to 16. The values calculated form equations from 12 to 16 were given in Table 2 along with the experimental values ($\theta_M$) evaluated in the current work for hcp phase. For a better appreciation, the Estimated Standard Deviations (E.S.Ds) in $\theta_M-\theta_c$ defined by $[(\theta_M-\theta_c)/\theta_M]^2/n$ are also given in Tables 2. In the hexagonal phase the E.S.D for $\theta_c$ evaluated from equation 14 is lower and the composition dependence of Debye temperature is best represented by the
equation 14 proposed by Sirdeshmukh [16] combining the high temperature approximation for the specific heat by Debyes theory and additivity of specific heats. While the composition dependence of Debye temperature of Cu$_{1-x}$Zn$_x$ alloys are best represented by equation 14 in hexagonal phase, the composition dependence of $\theta_M$ for mixed crystal systems with NaCl structure and CsCl structure and Al$_{1-x}$Mg$_x$ alloy system are best represented by equation 12.

**Table 2. Debye temperatures $\theta_M$(K) of hexagonal phase Cu$_{1-x}$Zn$_x$ system**

| Composition      | $\theta_M$ | $\theta_c$ | $\theta_c$ | $\theta_c$ | $\theta_c$ | $\theta_c$ |
|------------------|------------|------------|------------|------------|------------|------------|
|                  | Eq. 12     | Eq. 13     | Eq. 14     | Eq. 15     | Eq. 16     |
| Cu$_{20.80}$Zn$_{79.20}$ | 238(9)     | 231        | 232        | 242        | 234        | 239        |
| Cu$_{18.00}$Zn$_{82.00}$ | 237(6)     | 229        | 230        | 239        | 232        | 236        |
| Cu$_{15.70}$Zn$_{84.30}$ | 234(7)     | 228        | 229        | 237        | 230        | 234        |
| Cu$_{13.90}$Zn$_{86.10}$ | 232(7)     | 226        | 227        | 235        | 229        | 232        |
| Cu$_{12.90}$Zn$_{87.10}$ | 228(6)     | 221        | 221        | 223        | 221        | 219        |
| Cu$_{12.50}$Zn$_{87.50}$ | 221(6)     | 220        | 220        | 222        | 221        | 219        |
| Cu$_{10.90}$Zn$_{88.10}$ | 220(6)     | 220        | 220        | 221        | 220        | 218        |
| Cu$_{11.40}$Zn$_{88.60}$ | 219(8)     | 220        | 220        | 221        | 220        | 217        |
| Cu$_{9.60}$Zn$_{89.40}$ | 216(3)     | 219        | 219        | 220        | 219        | 216        |
| E.S.D. of        | ($\theta_c-\theta_M$) | 0.022 | 0.020 | 0.013 | 0.016 | 0.014 |

4.1 Gruneisen constant from Debye temperatures

Bansigir [5] had shown that log$\theta$-logV plot for a family of crystals is linear and its slope represents the mean Gruneisen constant for the family of crystals. He applied this concept to data for metals and alkali halides with NaCl structure and obtained reasonable values for the Gruneisen constant. The log$\theta$-logV plots for the hexagonal phases of Cu$_{1-x}$Zn$_x$ alloys were shown figure 3.

![Figure 3 Plot of log$\theta$ versus logV for hexagonal phase Cu$_{1-x}$Zn$_x$ system](image)

In this plot Debye temperature values obtained in the present investigation have been used. These plots are nearly linear. From the slopes of these plots the Gruneisen constants are obtained. In terms of experimentally observed quantities, the Gruneisen parameter is given by equation 10. The values of [eq.10] $\gamma$ evaluated from the slopes of log$\theta$-logV plot of the hexagonal phase of Cu$_{1-x}$Zn$_x$ alloy is 1.3. The value of Gruneisen parameter from the slope of the plot log$\theta$-logV for the entire Cu$_{1-x}$Zn$_x$ system

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is 1.35. The comparison of the values of Gruneisen parameter is made in the light of the following points; (i) strictly speaking, each crystal will have its own Gruneisen constant and this method assumes a common Gruneisen constant for the entire solid solution system. (ii) it is an approximate method. The variation of $\theta$ with the volume of a given material is implied in Eq. (11) whereas in the method of Bansigir [5], the relation of $\theta$ with the volume of different materials in a family is implied and the two are assume to be the same. In observation of these assumptions, the method can give only an order of magnitude agreement with thermal $\gamma$. Balaiah (15) applied this method to obtain $\gamma$ values for CsCl-CsBr and NH4Cl-NH4Br mixed crystal systems. Sirdeshmukh and Rao (16) and Purushotham (17-31) cautioned that this method has to be used with care. Keeping in view the above points, the values obtained for $\gamma$ for Cu$_{1-x}$Zn$_x$ alloy system are fairly in agreement with the thermal Gruneisen constants 2.14 and 2.75 for the Cu and Zn metals respectively.

5. Conclusions

X-ray determination of Debye temperature and Gruneisen constant values of Cu$_{1-x}$Zn$_x$ alloys have been reported. Values of $\theta_m$ for Cu$_{1-x}$Zn$_x$ alloys agree well with $\theta$ obtained from Kopp-Neumann relation and other four relations composition dependence relation, specific heat relation, empirical relation, Gril and Mittra relation. Gruneisen constant of hcp phase Cu$_{1-x}$Zn$_x$ alloys have been calculated using above five relations connecting it with the X-ray Debye temperature. The results on Cu$_{1-x}$Zn$_x$ alloys are reported for the first time.

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