Int. J. Chem. Sci.: 10(2), 2012, 873-880
ISSN 0972-768X
www.sadgurupublications.com

X-RAY DETERMINATION OF THE DEBYE-WALLER FACTORS AND DEBYE TEMPERATURE IN HEXAGONAL Cu_{1-X}-Zn_X ALLOYS

E. PURUSHOTHAM[*]

Department of Physics, Kakatiya University, WARANGAL – 506 009 (A.P.) INDIA

ABSTRACT

The anisotropic Debye-Waller factors and Debye temperatures of zinc rich Cu_{1-x} Zn_x alloys have been obtained from X-ray intensities. The intensities have been measured with Philips 3020 diffractometer fitted with a proportional counter using filtered Cukα. radiation at room temperature and have been corrected for thermal diffuse scattering. The anisotropy observed in the values of Debye-Waller factors of hexagonal zinc rich Cu_{1-x} Zn_x alloys conform to the trend observed in the anisotropy of Debye-Waller factors of hexagonal metals. The Debye temperatures obtained in the present investigation have been compared with the values of Debye temperature calculated from Kopp-Neumann relation.

Key words: X-ray diffraction, Debye-Waller factor, Vacancy formation energy.

INTRODUCTION

The relations between the anisotropy in physical properties have been discussed by Wooster[1], Boas and Mackenzie[2]. These discussions do not include the anisotropy of the Debye-Waller factors. The Debye-Waller factors are anisotropic in anisotropic crystals. Thus, hexagonal crystas have two principal Debye-Waller factors B_a and B_c associated with the 'a' and 'c' directions. The anisotropy in the values of B_a and B_c for several hexagonal close-packed (hcp) metals have been studied by earlier workers[3-7]. But such studies on the hexagonal alloys are scanty. In the present investigation, the results of a systematic study on the anisotropy of Debye-Waller factors of nine hexagonal Cu_{1-x} Zn_x alloys are reported.

EXPERIMENTAL

Cu_{1-x} Zn_x alloys with different compositions were prepared from spectroscopically pure Cu and Zn metals by melting appropriate quantities in evacuated quartz tubes. During

---

[*] Author for correspondence; E-mail: psm45456@gmail.com

the process of melting the mixture was thoroughly stirred for homogenization. The final compositions have been arrived at after subjecting these alloys to spectroscopic analysis. The powder samples of all the alloys were obtained by gently filing the ingots with jeweller's file. The filings were passed through a 325 mesh screen. All the samples were annealed before making measurements.

X-ray measurements were made with a Philips 3020 diffractometer fitted with a proportional counter using Cukα radiation. The X-ray tube was operated at 40 KV and 25 mA. All measurements were made at room temperature. All measurable peaks corresponding to an angular values of 2θ values between 20^o and 120^o were recorded.

The number of reflections ranged from 11 to 13. For the purpose of measurements of intensities, slow scans were obtained at a scanning speed of 0.5^o per minute. The integrated intensities have been corrected for thermal diffuse scattering using the method of Chipman and Paskin[8]. The absorption correction for a flat sample is angle independent and hence can be included in the scale factor. The porosity effect can also be lumped with the scale factor. The surface roughness effect becomes significant only at $2\theta < 20^o$, the reflections used in these studies have $2\theta > 20^o$. The Debye-Waller factors and Debye temperatures were determined following standard procedures.

Analysis of data

$Cu_{1-x}\,Zn_x$ alloys with different compositions belong to hexagonal close packed structure.The integrated intensity of Bragg reflection from a hexagonal cell may be written as follows[9-11].

$$I_0 = CI_c\exp\{-(4\pi\sin\theta/\lambda)^2[\langle u_{\parallel}^2\rangle \cos^2\psi + \langle u_{\perp}^2\rangle \sin^2\psi]\} \qquad ...(1)$$

Where c is a constant, I_c is the calculated intensity. $\langle u_{\parallel}^2\rangle$ and $\langle u_{\perp}^2\rangle$ refer to the components of the vibrational amplitude projected onto the hexagonal axis and the basal plane respectively. ψ is the angle between the diffraction vector and the hexagonal axis and λ the wavelength. The calculated intensity I_c is given by –

$$I_c = L_pJF^2 \qquad …(2)$$

The structure factors for fcc lattice is given by -

$$\begin{aligned} &F^2 = 16\,f^2 \text{ for h,k,l are all even} \\ &F^2 = 16\,f^2 \text{ for h,k,l are all odd} \qquad …(3) \\ &F^2 = 0 \text{ for h,k,l mixed} \end{aligned}$$

For the hexagonal close-packed structure, the structure factors are given by -

$$\left.\begin{array}{ll} F^2_{hkl} = 4\,f^2 \text{ for } h + 2k = 3n, & l = \text{even} \\ F^2_{hkl} = 3\,f^2 \text{ for } h + 2k = 3n \pm 1, & l = \text{odd} \\ F^{\,2}_{hkl} = f^2 \text{ for } h + 2k = 3n \pm 1, & l = \text{even} \end{array}\right\} \quad \ldots(4)$$

Where f is the atomic scattering factor for the $Cu_{1-x}\,Zn_x$ alloy,

$$<f> = X_{Cu}\,f_{Cu} + X_{Zn}\,f_{Zn} \quad \ldots(5)$$

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 are calculated from the atomic scattering factors given by Cromer and Waber[12]. These are corrected for anomalous dispersion[13]. $<u_{\parallel}^2>$ and $<u_{\perp}^2>$ are obtained from a least squares analysis of the logarithmic form of Eq. (1). From these, the directional Debye-Waller factors $B_{\perp}$ and $B_{\parallel}$ were obtained from the equations -

$$B_{\perp} = 8\pi^2 < u_{\perp}^{\,2} >, \quad B_{\parallel} = 8\pi^2 < u_{\parallel}^{\,2} > \quad \ldots(6)$$

The mean Debye-Waller factor $\overline{B}$ is given by -

$$B = (2B_{\perp} + B_{\parallel})/3 \quad \ldots(7)$$

The directional Debye temperatures $\theta_{\perp}$, $\theta_{\parallel}$ and mean Debye temperature θ_M were obtained from $B_{\perp}$, $B_{\parallel}$ and $\overline{B}$, respectively using the Debye-Waller theory[11] relation,

$$\begin{array}{l} B = (6h^2/M\,k_B\,\theta_M)\,W(X) \\ B_{\perp} = (6h^2/M\,k_B\,\theta_{\perp})\,W(X) \\ B_{\parallel} = (6h^2/M\,k_B\,\theta_{\parallel})\,W(X) \end{array} \quad \ldots(8)$$

where h is the Planck's constant, k_B the Boltzmann constant, M the atomic weight and θ_M the Debye temperature. The function W(X) is given by -

$$W(X) = [\phi(X)/X + (1/4)] \quad \ldots(9)$$

where $X = \theta_M/T$, T is the temperature of the crystal and $\phi(X)$ is the Debye function.

The values of W(X) for a wide range of X can be obtained from standard tables[14]. The data on Cu and Zn has been processed by assuming isotropic amplitude of vibration.

RESULTS AND DISCUSSION

The values of B_a and B_c for zinc rich $Cu_{1-x}Zn_x$ hexagonal alloys are given in Table 1. The values of mean Debye temperature (θ_M) obtained in the present investigation and the values of Debye temperature (θ) obtained from Kopp-Neumann relation are also included in Table 1 for comparison.

Table 1: Values of Debye-waller factors (B), Debye temperatures (θ_M) and energy of vacancy of formation (E_f) of Cu_{1-x}-Zn_x alloy

Composition x	C/a	B_c (Å^2)	B_a (Å^2)	B_{obs} (Å^2)	B_c/B_a	θ_c (K)	θ_a (K)	θ_M (K)	Kopp-Neumann θ (K)	E_f
79.40	1.51	1.03 ± 0.11	0.90 ± 0.12	0.95 ± 0.12	1.13	228 ± 5	243 ± 9	238 ± 8	231	0.63
82.30	1.56	1.06 ± 0.12	0.91 ± 0.11	0.96 ± 0.11	1.17	225 ± 4	243 ± 6	237 ± 5	229	0.62
84.50	1.59	1.07 ± 0.11	0.93 ± 0.11	0.98 ± 0.11	1.14	224 ± 5	240 ± 5	234 ± 5	228	0.59
86.2 0	1.63	1.11 ± 0.13	0.94 ± 0.12	1.01 ± 0.12	1.17	220 ± 3	238 ± 11	232 ± 9	226	0.56
97.10	1.80	1.56 ± 0.11	0.85 ± 0.11	1.09 ± 0.11	1.83	184 ± 4	250 ± 8	228 ± 6	221	0.52
97.60	1.81	1.77 ± 0.12	0.89 ± 0.21	1.18 ± 0.18	1.98	173 ± 4	245 ± 10	221 ± 8	220	0.48
98.10	1.82	1.79 ± 0.11	0.90 ± 0.11	1.20 ± 0.11	1.99	172 ± 26	244 ± 8	220 ± 14	220	0.47
98.70	1.83	1.80 ± 0.12	0.91 ± 0.13	1.21 ± 0.12	1.99	171 ± 4	242 ± 9	219 ± 8	220	0.46
99.50	1.84	1.86 ± 0.11	0.93 ± 0.22	1.24 ± 0.18	2.00	169 ± 17	240 ± 4	216 ± 9	219	0.45

The values of c/a for the alloys given in Table 1 are taken from Pearson[15]. The composition dependence of B_{obs} (experimental value of Debye-Waller factor) is shown in Fig. 1 for Cu_{1-x}-Zn_x alloys system. It is observed that the B_{obs} versus composition plot is non-linear with negative deviation from linearity. The experimental values of the Debye temperature are plotted as the function of composition in the Fig. 2. For the Cu_{1-x}-Zn_x alloys system the composition dependence of the Debye-temperature show a slight positive deviation from linearity.

In hcp crystals, the ideal c/a ratio is 1.633. Such a crystal will be nearly isotropic. A larger c/a ratio indicates weakening of interatomic forces in the 'c' direction. Since the Debye-Waller factor or atomic amplitudes of vibration reflects the interatomic bonding, the B_c/B_a ratio is expected to be > 1 for crystals with c/a > 1.633 while $B_c/B_a \sim 1$ for crystals with c/a close to 1.633.

Watanabe et al.[3] and Sirdeshmukh et al.[16], noted this feature in their study of several hexagonal metals. Further, Sirdeshmukh et al.[16], plotted a curve between B_c/B_a and these two crystals. In all other cases, c/a ~ 1.63 and B_c/B_a values are also ~ 1. No significance can be given to the cases where B_c/B_a is slightly larger than 1 while c/a values are slightly less than 1.63. This is obviously due to the errors in the Debye-Waller factors.

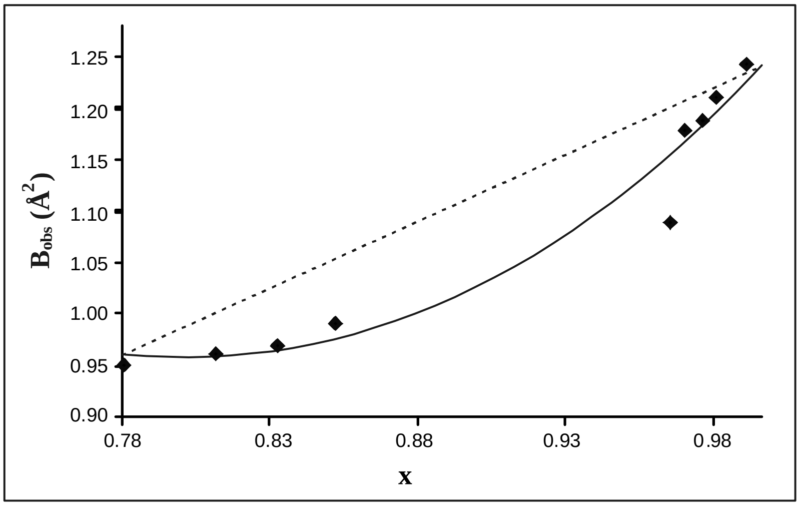

Fig. 1: Plot of Debye-Waller factor (B_{obs}) vs composition (x) for hexagonal Cu_{1-x}-Zn_x alloys system

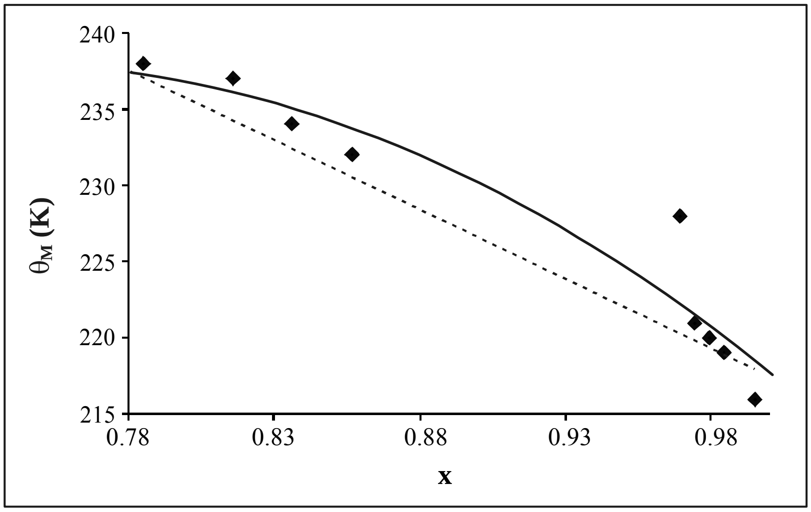

Fig. 2: Plot of Debye temperature (θ_M) vs composition (x) for Cu_{1-x}-Zn_x alloys

Glyde[17] derived the following relation between the energy of vacancy formation (E_f) and the Debye temperature (θ) of a solid. The relation is –

$$E_f = A\,(k/\hbar)^2\,M\theta^2a^2 \qquad \ldots(10)$$

where a is the interatomic spacing, A is a constant shown to be equal to 1.17 x 10^{-2}, M the molecular weight and h and k are the Plank's and the Boltzmann's constants respectively. Glyde recommended the use of X-ray based values for use in Eq. (10). The validity of Eq. (8) was verified for a number of fcc, bcc and hcp metals[18]. Therefore, the X-ray Debye temperatures obtained in the present work have been used to study the variation of vacancy formation energy as a function of lattice strain in $Cu_{1-x}Zn_x$ alloys. The values of vacancy formation energies are also included in Table 1.

CONCLUSION

The results on the X-ray determination of directional amplitudes of vibration, Debye-Waller factor and Debye temperature of Cu_{1-x} Zn_x alloys have been reported. The results on Cu_{1-x} Zn_x alloys are reported for the first time. Within the limits of experimental errors, the anisotropy observed in these parameters is negligible. Values of θ_M for Cu_{1-x} Zn_x alloys agree well with θ obtained from Kopp-Neumann relation. The values of vacancy formation energy (E_f) are estimated for Cu_{1-x} Zn_x alloys.

ACKNOWLEDGEMENT

Author is thankful to University Grants Commission, New Delhi, for the financial support through special assistance programme (No. F. 530/8/DRS/2009 (SAP-1)).

REFERENCES

1. W. A. Wooster, A Text Book of Crystal Physics, Camebridge University Press, Camebridge (1938).
2. W. Boas and J. K. Mackenzie, Prog. Met. Phys., **2**, 90 (1950).
3. Y. Watanabe, H. Iwasaki and S. Ogawa, Japan J. Appl. Phys., **10**, 786 (1971).
4. E. F. Skelton and J. L. Katz, Phys. Rev., **171**, 801 (1968).
5. N. Gopi Krishna, D. B. Sirdeshmukh, B. Rama Rao and B. J. Beaudry, K. A. Gschneidner, Ind. J. Pure Appl. Phys., **24**, 324-326 (1986).
6. N. Gopi Krishna, D. B. Sirdeshmukh, Ind. J. Pure Appl. Phys., **25**, 503 (1987).
7. M. Shankar Narayana, N. Gopi Krishna and D. B. Sirdeshmukh, Acta Cryst. A.**, 57,** 217 (2001).
8. D. R. Chipman and A. Paskin, J. Appl. Phys., **30**, 1938 (1959).
9. M. Blackman, Acta Cryst., (Denmark), **9**, 734-758 (1956).
10. H. Lipson, International Tables for X-ray Crystallography, **2** (Kynoch Press, Birminghm) (1959).
11. R. W. James, The Optical Principles of the Diffraction of X- rays (Bell and Sons, London) (1967).
12. D. T. Cromer and J. T. Waber, Acta Crystallogr (Denmark), **18**, 104-109 (1965).
13. D. T. Cromer and D. Liberman, J. Chem. Phys., **53**, 1891 (1970).
14. International Tables for X-ray Crystallography, **Vol. III,** (Birmingham Kynoch press) (1968).
15. W. B. Pearson, A Hand Book of Lattice Spacing and Structure of Metals and Alloys (Pergon Press, Oxford) (1956).
16. D. B. Sirdeshmukh, L. Sirdeshmukh and K. G. Subhadra, Micro-and Macro-Properties of Solids (Springer- Verlag Berlin Heidlberg) (2006).

17. H. R. Glyde, J. Phys. Chem. Solids, (G.B) **28**, 2061 (1967).

18. D. B. Sirdeshmukh, L. Sirdeshmukh and K. G. Subhadra, Micro-and Macro-Properties of Solids, (Springer Series in Material Science) (2006).

Accepted : 10.01.2012