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Mean Square Amplitudes of vibration and Associated Debye temperatures of Mg, Zn and Cd

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Abstract

The directional mean square amplitudes of vibration Debye-Waller factor and associated Debye temperatures of hexagonal Mg, Zn and Cd have been obtained from X- ray integrated intensities. The integrated intensities have been measured with a Philips 3020 powder diffractometer fitted with a proportional counter using filtered CuKα □ radiation at room temperature and have been corrected for thermal diffuse scattering. Within the limits of experimental errors, the anisotropy observed in these parameters. The experimental values of directional Debye temperature have been compared with corresponding values obtained from theoretical calculations. Vacancy formation energies of Mg, Zn and Cd have been estimated using a relation connecting it with the X-ray Debye temperature.

Keywords :X-ray diffraction, Debye temperature , hcp element vacancy formation energy.

1 Introduction

The amplitudes of vibration and Debye temperature are important solid state parameters. These parameters are directional in anisotropic crystals. There is considerable theoretical and experimental work on the determination of mean square amplitudes of vibration and Debye temperatures of hexagonal close packed (hcp) metals. Mean square amplitudes of vibration and directional Debye temperatures of hcp rare earth metals were reported by Gopi Krishna et al [1,2]. Gopi Krishna and Sirdeshmukh [3] compiled directional Debye-Waller factors of several hcp elements. Shankarnarayana et al [4] reported Debye-Waller factors for hcp elements titanium(Ti), zirconium (Zr), ruthenium(Ru), thulium(Tm) and hafnium(Hf). Sirdeshmukh et al [5] discussed the anisotropy in Debye-Waller factors of seventeen hcp metals. Singh and Varshini [6] made theoretical calculation of directional X-ray Debye temperatures of several hcp metals. They made a comparison of their calculated results with experimental results. There are no X-ray data on the amplitudes of vibration and Debye temperature of Mg, Zn and Cd. The purpose of this communication is to report the results of an X-ray investigation to determine the mean square amplitudes of vibration and associated Debye temperatures of Mg, Zn and Cd.

2 Experimental

The metal samples were obtained from a commercial source and were available in the form of small ingots. Fine filings were obtained from the ingots with the help of a jeweller's file. The filing was carried out slowly. The filings were passed through a 325 mesh screen. 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 25mA. All measurements were made at room temoerature. The extra reflections in the diffraction patterns indicate the presence of some impurities. These slow scans were obtained at a scanning speed of 0.5° per minute for the purpose of measurement of intensities. The number of reflections recorded ranged from 15 to 20. The procedure for sample preparation, instrumental conditions for recording intensities and details of various corrections applied are given in earlier papers [1,6].

3 Analysis of Data

Mg, Zn and Cd belong to hexagonal close packed structure.The integrated intensity of Bragg reflection from a hexagonal cell may be written as follows [7-9]

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

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

$$I_c = L_pJF^2, \qquad (2)$$

L_p is the Lorentz-Polarization factor, J the multiplicity factor and F the structure factor. The structure factors are given by

$$\begin{aligned} F^2_{hkl} &= 4f^2 \text{ for } h + 2k = 3n, & l &= \text{even}, \\ F^2_{hkl} &= 3f^2 \text{ for } h+2k = 3n \pm 1, & l &= \text{odd}, \qquad (3) \\ F^2_{hkl} &= f^2 \text{ for } h+2k = 3n \pm 1, & l &= \text{even}, \end{aligned}$$

f is the atomic scattering factor. The structure factors are calculated from the atomic scattering factors given by Cromer and Waber [10]. These are corrected for anomalous dispersion [11]. $<u_{\parallel}^2>$ 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

$$B_{\perp} = 8\pi^2 < u_{\perp}^2 >, \quad B_{\parallel} = 8\pi^2 < u_{\parallel}^2 > \qquad (4)$$

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

$$\bar{B} = (2B_{\perp} + B_{\parallel})/3 \qquad (5)$$

The directional Debye temperatures $\theta_{\perp}$, $\theta_{\parallel}$ and mean Debye temperature θ_M were obtained from $B_{\perp}$, $B_{\parallel}$ and $\bar{B}$, respectively using the Debye-Waller theory [9] relation,

$$\begin{aligned} \bar{B} &= (6h^2/M k_B \theta_M)\, W(X) \\ B_{\perp} &= (6h^2/M k_B \theta_{\perp})\, W(X) \qquad (6) \\ B_{\parallel} &= (6h^2/M k_B \theta_{\parallel})\, W(X) \end{aligned}$$

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

$$W(X) = [\, \phi(X)/X + (1/4) \,], \qquad (7)$$

$X = \theta_M/T$, 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 [12].

4 Results and discussion

The values of the mean square amplitudes of vibration, Debye-Waller factor and the Debye temperature of Mg, Zn and Cd obtained in the present study are given in Table 1. The c/a values are also given in Table 1 and they are greater than the ideal value of 1.63 for hcp elements. Keeping the limits of error in view, it is seen that the anisotropy in the values of the amplitude of vibration is slight in the case of Mg and $<u_{\parallel}^2>$ almost twice of $<u_{\perp}^2>$ in the case of both Zn and Cd. As a consequance, the directional Debye-Waller factors and Debye temperatures also exhibit only a slight anisotropy in the case of Mg and twice in the case of Zn and Cd. This is in conformity with the observation made by Sirdeshmukh et al [5] in several hexagonal metals. They observed that the anisotropy is significant only in those cases where the c/a ratio differs significantly from the ideal value 1.63. The directional Debye temperature obtained in the present work are of the same order as those obtained from theoretical calculation using elastic constant data by Singh and Varshni [6]. Values of Debye temperature obtained from specific heat data (θ_D) and elastic constant data (θ_E) [13] are given for comparison. The values of θ_M obtained in the present work for Mg, Zn and Cd agree well with those obtained from specific heat data and elastic constant data. It may, however, be mentioned that exact agreement is not expected between the values of θ_M and θ_D, θ_E (13).

The values of vacancy formation energies are useful in understanding the diffusion mechanism in pure metals as the vacancy mechanism is the dominant mechanism for diffusion in most pure metals. As such, an attempt has been made to estimate the values of the energy of vacancy formation (E_f) for Mg, Zn and Cd.

Glyde [14] derived the following relation between the energy of vacancy formation (E_f) and the Debye temperature (θ) of a solid;

$$E_f = A(k/\hbar)^2 M\theta^2 a^2 \qquad (8)$$

a is the interatomic spacing, A a constant shown to be equal to 1.17×10^{-2}, M the atomic weight and h and k are the Plank's and the Boltzmann's constants respectively. Glyde [14] recommended the use of X-ray based values for use in Eq. (8). The validity of Eq.(8) was verified for a number of fcc,bcc and hcp metals [15-17]. Therefore, the X-ray Debye temperatures obtained in the present work have been used to estimate vacancy formation energies for Mg, Zn and Cd. The estimate vacancy formation energies for Mg, Zn and Cd are given in table 1. The experimental values of E_f are not available for comparison.

5 Conclusion

The results on the X-ray determination of directional amplitudes of vibration, Debye-Waller factor and Debye temperature of Mg, Zn and Cd have been reported the results on Mg, Zn and Cd are reported for first time. Within the limits of experimental errors, the anisotropy observed in these parameters is not negligible. Values of θ_M for Mg, Zn and Cd agree well with θ_D and θ_E obtained from spesific heats and elastic constants respectively. The values of vacancy formation energy (E_f) are estimated for Mg, Zn and Cd.

Table 1. Values of Mean square amplitude of vibration, Debye-Waller factor and Debye temperature of Mg, Zn and Cd

Parameter	**c/a**	**$\langle u_{\parallel}^2 \rangle$ (Å)**	**$\langle u_{\perp}^2 \rangle$ (Å)**	**$B_{\parallel}$ (Å)**	**$B_{\perp}$ (Å)**	**$\theta_{\parallel}$ (K)**	**$\theta_{\perp}$ (K)**	**θ_M (K)**	**E_f (eV)**
Mg	1.62	0.0199(1)	0.0185(1)	1.63(1)	1.44(1)	303(3)	315(3)	311(3)	0.51
Zn	1.86	0.0242(1)	0.0129(1)	2.18(1)	0.89(1)	167(2)	229(2)	208(2)	0.42
Cd	1.89	0.0391(2)	0.0141(3)	3.05(2)	1.17(17)	100(8)	166(8)	144(8)	0.44

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