Indian J. Phys. **84** (**7**) 887-893 (2010)

Note

Effect of lattice strain on the Debye-Waller factors of Mg, Zn and Cd

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Received 20 August 2009, accepted 25 January 2010

Abstract : Lattice strains in Mg, Zn and Cd powders produced by grinding have been analyzed by X-ray powder diffraction. The lattice strain (ε) and Debye-Waller factor (B) are determined from the half-widths and integrated intensities of the Bragg reflections. In all three cases *viz.* Mg, Zn and Cd, the Debye-Waller factor is found to increase with the lattice strain. From the correlation between the strain and effective Debye-Waller factor, the Debye-Waller factors for zero strain have been estimated for Mg, Zn and Cd. The variation of energy of vacancy formation as a function of lattice strain has been studied.

Keywords : X-ray diffraction, lattice strain, Debye-Waller factor, vacancy formation energy.

PACS Nos. : 61.10.NZ, 63.20.-e, 65.90.+i

The Debye-Waller factor is an important lattice dynamical property. Although there is considerable X-ray work on the Debye-Waller factors of Mg, Zn and Cd [1–4]. It is interesting to study the effect of lattice strains on the Debye-Waller factors of these metals. Inagaki *et al* [5,6] showed that in several non-metallic powders, the strains produced during grinding have a significant effect on the Debye-Waller factors measured from X-ray diffraction intensities. Sirdeshmukh *et al* [7] observed the effect of lattice strains on the Debye-Waller factors in semiconductor powder materials. Gopi Krishna and Sirdeshmukh [8] studied the effect of lattice strains on the Debye-Waller factor of ytterbium metal. In the present investigation the results of a systematic study of the effect of lattice strains on the Debye-Waller factors of hexagonal Mg, Zn and Cd metals are reported.

The powder samples were obtained by gently filing highly pure Mg, Zn and Cd

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metal ingots with a jeweller's file. A part of this powder was used to prepare the initial sample. The remaining powder was subjected to slow grinding in an agate mortar for 4, 8, 12, 16 and 20 hours to produce strains. X-ray diffractograms were recorded with the initial sample and with samples prepared after each spell of grinding. The diffractograms were obtained with a Philips CWU 3710 X-ray powder diffractometer in the 2θ range 20–120° using filtered CuK_α at a goniometer speed of 0.5° per minute and a chart speed of 20 mm/min. All the measurements were made at room temperature. The observed integrated intensities have been corrected for thermal diffuse scattering using the method of Chipman and Paskin [9].

The procedure for the determination of directional mean-square amplitudes of vibration $\langle u_{\|}^2 \rangle$ and $\langle u_{\perp}^2 \rangle$ from the intensity data and the estimation of associated errors is similar to what has been discussed by Gopi Krishna *et al* [10]. The average mean square amplitude $\langle u_{av}^2 \rangle$ can be obtained from the relation,

$$\langle u_{av}^2 \rangle = 1/3(\langle u_{\|}^2 \rangle + 2\langle u_{\perp}^2 \rangle) \tag{1}$$

and the directional Debye-Waller factors $B_\perp$ and $B_{\|}$ were obtained from the equations

$$\left.\begin{aligned} B_\perp &= 8\pi^2 < u_\perp^2 > \\ B_{\|} &= 8\pi^2 < u_{\|}^2 > \end{aligned}\right\}. \tag{2}$$

The mean Debye-Waller factor B is given by

$$B = (2B_\perp + B_{\|})/3.$$

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

$$\left.\begin{aligned} B &= (6h^2/Mk_B\theta_M)W(X) \\ B_\perp &= (6h^2/Mk_B\theta_\perp)W(X) \\ B_{\|} &= (6h^2/Mk_B\theta_{\|})W(X) \end{aligned}\right\} \tag{3}$$

where h is the Planck's constant, k_B the Boltzmann constant, M the atomic weight. The function $W(X)$ is given by

$$W(X) = [\phi(X)/X + (1/4)] \tag{4}$$

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 [12].

The lattice strains were determined from the plot of $\beta\cos\theta/\lambda$ against $\sin\theta/\lambda$ following standard procedures [13]. The measured half-widths were corrected for instrumental broadening with reference to a pure strain-free silicon powder. The variation

of particle size with grinding time is within the limits of experimental errors. This shows that while the grinding is enough to create strains, it does not affect the particle size to a measurable extent. A typical Hall-Williamson plot is shown in Figure 1 for Mg after grinding for 16 hours.

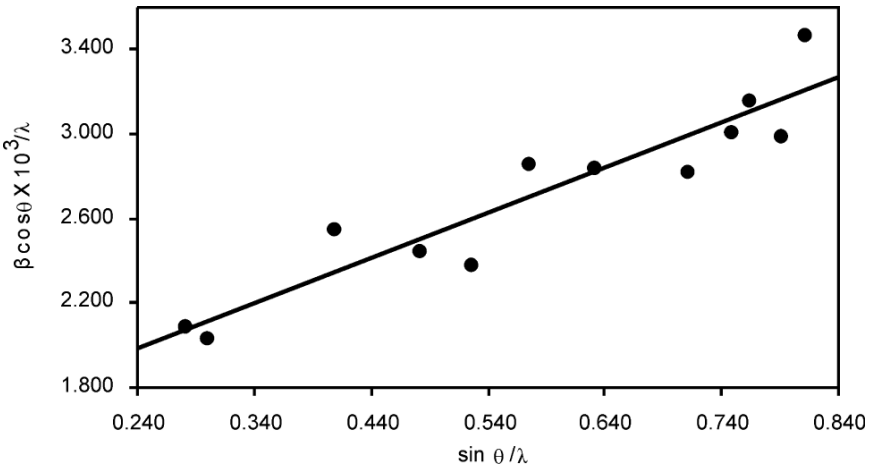

Figure 1. Plot of $\beta\cos\theta/\lambda$ *vs.* $\sin\theta/\lambda$ for Mg after grinding for 16 hours.

The values of the lattice strain, root mean square amplitude of vibrations, Debye-Waller factor and Debye temperature of Mg, Zn and Cd powders, ground for different durations, obtained in the present study are given in Table 1. Although, values of Deby-Waller factor, amplitude of vibration and Debye temperature in the '*a*' and '*c*' directions have been determined separately, the average values of these quantities are given in Table 1. As the objective of the present work is to investigate the strain dependence of Debye-Waller factors, the variation of the lattice strain (ε) and Debye-Waller factor (B) for different grinding times for all the three hcp metals Mg, Zn and Cd is shown in Figure 2(a-i). Both lattice strain and Debye-Waller factor increase with grinding time. This is similar to the observations of Inagaki *et al.* [5,6], Sirdeshmukh *et al* [7] and Gopi Krishna and Sirdeshmukh [8]. In all three cases, the Debye-Waller factor increases with grinding time and lattice strain in a slightly non-linear fashion. An extrapolation of the *B versus* ε curve to ε = 0 gives the values of Debye-Waller factor 1.46 Å^2, 1.26 Å^2 and 1.70 Å^2 for Mg, Zn and Cd respectively. All these zero-strain values of Debye-Waller factor are less than the values for the initial samples. The zero strain Debye-Waller factors of 1.46 Å^2 and 1.26 Å^2 for Mg and Zn are close to the values of 1.42 Å^2 and 1.27 Å^2 obtained by Watanabe *et al* [1] and Skelton and Katz [2], respectively, using single crystal X-ray diffraction. The zero-strain value of Debye-Waller factor of 1.70 Å^2 for Cd obtained in the present work agrees well with 1.77 Å^2 obtained by Rossmanith [3] using single crystal X-ray diffraction. Thus, the Debye-

Table 1. Values of lattice strain (ε), mean Debye-Waller factor (B), root mean square amplitudes of vibration $< u_{av} >$, mean Debye temperature (θ_M) and energy of vacancy formation (E_f) of strained Mg, Zn and Cd powders.

Metal	Grinding time	$\in \times 10^3$	u_{av} (Å)	B_{av} (Å^2)	θ_M (K)	E_f (eV)
Mg	0	0.28	0.14 (4)	1.5 (2)	311 (3)	0.50
	4	0.46	0.14 (4)	1.5 (1)	307 (5)	0.49
	8	0.64	0.15 (3)	1.7 (1)	293 (3)	0.44
	12	0.85	0.15 (4)	1.8 (2)	281 (13)	0.40
	16	1.07	0.16 (4)	2.0 (2)	268 (9)	0.37
	20	1.27	0.17 (4)	2.4 (1)	247 (6)	0.34
Zn	0	0.15	0.13 (6)	1.3 (3)	208 (23)	0.42
	4	0.24	0.13 (7)	1.4 (4)	204 (31)	0.41
	8	0.36	0.14 (4)	1.4 (1)	198 (10)	0.38
	12	0.45	0.14 (6)	1.6 (3)	185 (17)	0.33
	16	0.57	0.15 (6)	1.8 (3)	179 (17)	0.31
	20	0.65	0.16 (5)	2.0 (2)	168 (9)	0.28
Cd	0	1.19	0.15 (7)	1.8 (4)	144 (25)	0.43
	4	1.75	0.15 (6)	1.8 (3)	143 (14)	0.43
	8	2.96	0.16 (7)	1.9 (4)	138 (16)	0.40
	12	3.26	0.16 (7)	2.0 (3)	131 (12)	0.36
	16	3.60	0.17 (6)	2.2 (3)	126 (8)	0.33
	20	4.02	0.18 (7)	2.5 (4)	121 (11)	0.31

Waller factors of Mg, Zn and Cd powder samples carry an effect due to lattice strain. While comparing the Debye-Waller factors calculated from the lattice dynamical models with experimental results, Vetelino *et al* [14] have attributed the difference to inaccuracies in the experimental values caused by neglecting the TDS corrections. The repeated grinding of the powder sample leads to lattice distortion which gives rise to microstrains in the lattice. These microstrains increase the contribution of static component of Debye-Waller factor. Thus both lattice strain and the observed Debye-Waller factor, which is the sum of static and thermal components, increase with grinding time. Thus, whenever Debye-Waller factors are determined from X-ray intensities on powder samples, it is desirable to make an estimate of the lattice strain and if the strain is large, a suitable correction is to be made as done in the present study. The Debye temperatures derived from the zero strain values of Debye-Waller factor of Mg, Zn and Cd are 315 K, 205 K, and 134 K, respectively. These values agree well with the values of 320 K [9], 222 K [10] and 143 K [11] obtained for Mg, Zn and Cd from the single crystal X-ray diffraction.

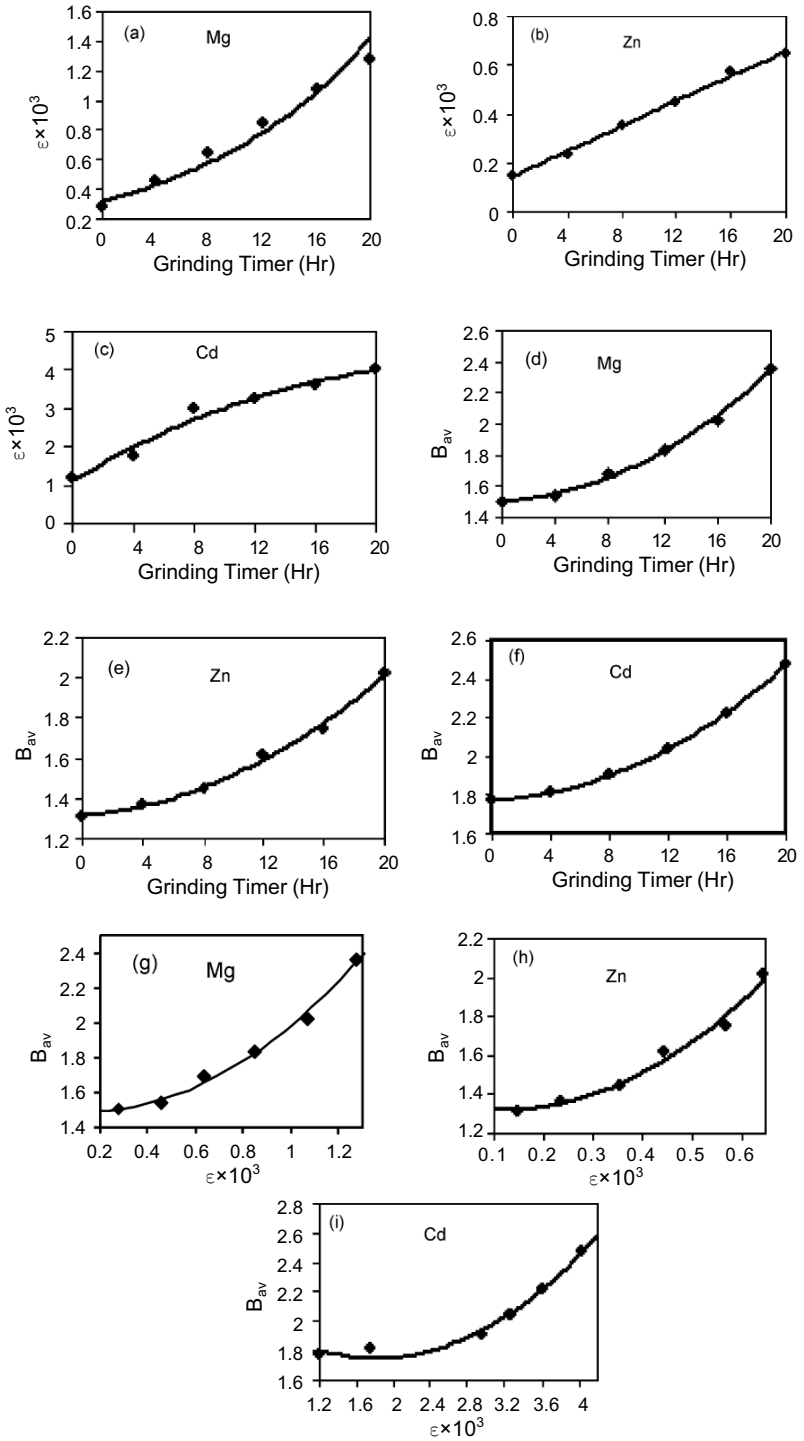

Figure 2 (a-i). Grinding time *vs.* lattice strain and Debye-Waller factor and lattice strain *vs.* Debye-Waller factor curves for Mg, Zn and Cd.

Glyde [15] derived the following relation between the energy of vacancy formation (E_f) and the Debye temperature (θ) of a solid. The relation is

$$E_f = A(k/\hbar)^2 \; M\theta^2 a^2 \tag{5}$$

where a is the interatomic spacing, A a constant shown to be equal to 1.17×10^{-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 in eq. (5). The validity of eq. (5) was verified for a number of fcc, bcc and hcp metals [16]. 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 Mg, Zn and Cd. The values of vacancy formation energies are also included in Table 1.

Mg, Zn and Cd powders were strained by grinding for 20 hours. From a study of X-ray diffractograms recorded at different stages of grinding, it is observed that grinding for 20 hours has no systematic effect on the particle size. However, the grinding produces lattice strain and also enhances the effective Debye-Waller factor. By an extrapolation of the plot between the Debye-Waller factor and the lattice strain, the zero strain Debye-Waller factors are obtained for Mg, Zn and Cd. The variation of energy of vacancy formation as a function of lattice strain has been studied.

Acknowledgments

The referee is thanked for several useful suggestions. The authors thank University Grants Commission, New Delhi, for financial assistance under special assistance programme (SAP) No. F.530/8/DRS/2009 (SAP-I).

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