

Characterization of Hexagonal Mg and Laves-phase MgZn₂ by Ultrasonic Technique

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The ultrasonic properties like ultrasonic attenuation, sound velocity in the hexagonal Mg and Laves phase MgB₂ have been studied along unique axis at room temperature. The second- and third order elastic constants (SOEC & TOEC) have been calculated for these compounds using Lennard–Jones potential. The velocities V_L and V_{S1} have maxima and minima, respectively, with 45° with unique axis of the crystal, while V_{S2} increases with the angle from unique axis. The inconsistent behavior of angle dependent velocities is associated to the action of second order elastic constants. Debye average sound velocities of these metals and alloys are increasing with the angle and has maximum at 55° with unique axis at room temperature. Hence when a sound wave travels at 55° with unique axis of these metals, then the average sound velocity is found to be the maximum. The value of acoustic attenuation of MgZn₂ is smallest in comparison to Magnesium. So, MgZn₂ is more ductile and purer than the others. The acoustic attenuation due to phonon-phonon interaction mechanism is predominant over total attenuation as a governing factor for thermal conductivity. The mechanical properties of MgZn₂ are better than that of Mg because MgZn₂ has high elastic constants and low acoustic attenuation. Results obtained, together with other well known physical properties, may expand future prospects for the application and study of these materials.

1. Introduction

Elastic properties of magnesium and its alloys have been extensively studied in the last several decades. For example, the elastic stiffness tensor of the single crystal Mg was determined through both experimental measurements [1-4] as well as theoretical predictions [5,6]. The distribution of crystallographic orientations, or texture, will significantly affect the effective elastic properties of a polycrystalline [7]. MgZn-based alloys display a rich variety of intermediate phases of varying structural complexity. The simplest one of the various Mg-Zn inter-metallic compounds is MgZn₂, which is a C14 hexagonal Laves phase [8].

Magnesium alloys have been used widely in various fields such as aerospace and transportation vehicles due to their high specific strength, low density, good damping capacity, capacity for casting, and recycling [9,10]. In order to further expand the application of magnesium alloys, joining processes, such as friction stir welding, tungsten inert gas welding, vacuum diffusion welding, reactive brazing, soldering, laser beam welding, and electron beam welding have been applied to weld magnesium alloys [11]. MgB₂ alloys are one of the most important structural

materials having high specific strength and used widely in automotive, communication, electronic and aerial industries [12]. The magnesium-zinc alloy system possesses the greatest precipitation hardening response of commercial Mg-based alloys due to the precipitation of a fine, rod-like precipitate termed [13].

The single crystalline elastic constants of the ternary Laves phase Mg (Cu, Zn₂) have been determined by the ultrasonic pulse-echo technique over the temperature dependence [14]. Z. H. Huang et. al. have focused on the micro-structural and tensile mechanical properties at ambient and elevated temperatures of magnesium alloys [15]. The electrochemical properties of MgZn₂ and other alloys have been evaluated by A. D. Sudholz [16].

The ultrasonic method offers the possibility to detect and characterize micro-structural properties as well as flaws in materials, controlling materials behavior based on physical mechanism to predict future performance of the materials. Various investigators have shown considerable interest on ultrasonic properties of metals and alloys. Wave propagation velocity is a key parameter in ultrasonic characterization and can provide information about crystallographic texture. The ultrasonic velocity is directly related to the elastic constants by the relationship $V = \sqrt{C/\rho}$, where C is the relevant elastic constants and ρ is the density of

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that particular material. Also ultrasonic attenuation is very important physical parameter to characterize the material, which is well related to several physical quantities like thermal conductivity, specific heat, thermal energy density, and higher order elastic constants [17,18]. The elastic constants provide valuable information about the bonding characteristic between adjacent atomic planes and the anisotropic character of the bonding and structural stability [19,20].

Therefore, in this work we predict the ultrasonic properties of hexagonal structured Mg and laves-phase MgB_2 at room temperature. The ultrasonic attenuation coefficient, acoustic coupling constants, higher order elastic constants, thermal relaxation time and ultrasonic wave velocities for these compounds for each direction of propagation of wave are calculated at 300K. The calculated ultrasonic parameters are discussed with related thermo-physical properties for the characterization of this metal and its alloy.

2. Theory

In the present investigation, the theory is divided into two parts:

2.1. Second and third order elastic constants

The second (C_{IJ}) and third (C_{IJK}) order elastic constants of material are defined by following expressions.

$$C_{IJ} = \frac{\partial^2 U}{\partial e_I \partial e_J}; \quad I \text{ or } J = 1, \dots, 6 \quad (1)$$

$$C_{IJK} = \frac{\partial^3 U}{\partial e_I \partial e_J \partial e_K}; \quad I \text{ or } J \text{ or } K = 1, \dots, 6 \quad (2)$$

Where, U is elastic energy density, $e_i = e_{ij}$ (i or $j = x, y, z, I = 1, \dots, 6$) is a component of strain tensor. Eqns. (1) and (2) leads six second and ten third order elastic constants (SOEC and TOEC) for the hexagonal close packed structure materials [17,21].

$$\left. \begin{aligned} C_{11} &= 24.1 p^4 C' & C_{12} &= 5.918 p^4 C' \\ C_{13} &= 1.925 p^6 C' & C_{33} &= 3.464 p^8 C' \\ C_{44} &= 2.309 p^4 C' & C_{66} &= 9.851 p^4 C' \end{aligned} \right\} \quad (3a)$$

$$\left. \begin{aligned} C_{111} &= 126.9 p^2 B + 8.853 p^4 C' & C_{112} &= 19.168 p^2 B - 1.61 p^4 C' \\ C_{113} &= 1.924 p^4 B + 1.155 p^6 C' & C_{123} &= 1.617 p^4 B - 1.155 p^6 C' \\ C_{133} &= 3.695 p^6 B & C_{155} &= 1.539 p^4 B \\ C_{144} &= 2.309 p^4 B & C_{344} &= 3.464 p^6 B \\ C_{222} &= 101.039 p^2 B + 9.007 p^4 C' & C_{333} &= 5.196 p^8 B \end{aligned} \right\} \quad (3b)$$

Where, $p = c/a$ is the axial ratio,

$$C' = \chi a / p^5,$$

$$B = \psi a^3 / p^3,$$

$$\chi = (1/8)[\{nb_0(n-m)\}/\{a^{n+4}\}],$$

$$\psi = -\chi / \{6 a^2(m+n+6)\},$$

m and n are integers,

and b_0 is the Lennard-Jones parameter.

2.2. Ultrasonic attenuation and allied parameters

The predominant causes for the ultrasonic attenuation in a solid at room temperature are phonon-phonon interaction (Akhieser loss) and thermo-elastic relaxation mechanisms. The ultrasonic attenuation coefficient ($\mathcal{A}$)_{Akh} due to phonon-phonon interaction and thermo-elastic relaxation mechanisms is given by the following expression [21,22].

$$(\mathcal{A}/f^2)_{\text{Akh}} = 4\pi^2 \left(3E_0 <(\gamma_i^j)^2> - <\gamma_i^j>^2 C_V T \right) \tau / 2 \rho V^3 \quad (4)$$

$$(\mathcal{A}/f^2)_{\text{Th}} = 4\pi^2 <\gamma_i^j>^2 kT / 2\rho V_L^5 \quad (5)$$

Where, f is the frequency of the ultrasonic wave, V the ultrasonic velocity for longitudinal and shear wave, V_L the longitudinal ultrasonic velocity, E_0 the thermal energy density, and γ_i^j Grüneisen number (i, j are the mode and direction of propagation).

The Grüneisen number for hexagonal structured crystal along $\langle 001 \rangle$ orientation or $\theta=0^\circ$ is direct consequence of second and third order elastic constants. $D = 3(3E_0 <(\gamma_i^j)^2> - <\gamma_i^j>^2 C_V T) / E_0$ is known as the acoustic coupling constant, which is the measure of acoustic energy converted to thermal energy. When the ultrasonic wave propagates through crystalline material, the equilibrium of phonon distribution is disturbed. The time for re-establishment of the equilibrium of thermal phonon distribution is called thermal

relaxation time (τ) and is given by following expression

$$\tau = \tau_s = \tau_L / 2 = 3k / C_V V_D^2 \quad (6)$$

Here τ_L and τ_s are the thermal relaxation times for longitudinal and shear wave, respectively; k and C_V are the thermal conductivity and specific heat per unit volume of the material, respectively. The Debye average velocity (V_D) is well related to longitudinal (V_L) and shear wave (V_{S1} , V_{S2}) velocities. The expressions for ultrasonic velocities are given in our previous paper [22]. The ultrasonic velocities have been used for the calculation of

ultrasonic attenuation and allied parameters in the chosen metals.

3. Results and Discussion

3.1. Higher order elastic constants

The unit cell parameters 'a' (basal plane parameter) and 'p' (axial ratio) for Mg and MgZn₂ are 3.19Å, 5.22Å and 1.627, 1.640, respectively [23,24,]. The value of m and n for chosen materials are 6 and 7. The values of b_0 are 5.5×10^{-65} erg cm⁷ and 1.6×10^{-62} erg cm⁷ Mg and MgZn₂, respectively. The SOEC and TOEC have been calculated for these compounds using Eqn. (3) and are presented in Table 1.

Table 1: Second and third order elastic constants (SOEC and TOEC) & Bulk Modulus (B) in the unit of 10^{10} Nm⁻² of Mg and MgZn₂ at room temperature.

	C ₁₁	C ₁₂	C ₁₃	C ₃₃	C ₄₄	C ₆₆	B
Mg	6.53	1.60	1.38	6.58	1.66	2.56	3.15
MgZn ₂	13.69	3.36	2.94	13.24	3.53	5.37	6.68
Mg[25]	6.09	2.38	2.21	6.72	1.76	1.86	3.61
Mg [26]	6.40	2.50	2.20	6.70	1.80		
Mg [27]	5.93	2.57	2.14	6.15	1.64		
MgZn ₂ [24]	13.41	4.36			5.78		
MgZn ₂ [27]	10.3	4.72	2.90	11.8	2.62		

	C ₁₁₁	C ₁₁₂	C ₁₁₃	C ₁₂₃	C ₁₃₃	C ₃₄₄	C ₁₄₄	C ₁₅₅	C ₂₂₂	C ₃₃₃
Mg	-106.53	-16.89	-3.54	-4.50	-22.23	-20.84	-5.25	-3.50	-84.29	-82.73
MgZn ₂	-223.34	-35.41	-7.55	-9.59	-48.10	-45.10	-11.18	-7.45	-176.71	-181.93

The calculated SOEC of Mg metal and its alloy are approximately the same as theoretical and experimentally values [24-27]. Actually they have based *ab-initio* local spin-density functional theory with generalized gradient corrections (GGA) approach to evaluate elastic constants, which is quite different from the present approach, although obtained SOEC are of the same order as others. Relative magnitude of C_{11} , C_{33} , C_{44} are well presented by our theoretical approach, which are in good agreement with theoretical and experimental results as shown in Table 1. The obtained values of the SOEC and TOEC are of the same order as previous experimental and theoretical values of other metallic alloys and metals [17, 28-32]. Hence, our theoretical approach to evaluate elastic

constants seems to be valid for these ferromagnetic metals. The bulk modulus (B) for these compounds can be calculated with the formula $B = 2(C_{11} + C_{12} + 2C_{13} + C_{33})/9$. The evaluated B for these metals is presented in Table 1.

3.2. Ultrasonic velocity and allied parameters

The density and thermal conductivity at room temperature have been taken from the literature [23,24]. The value of C_V and E_0 are evaluated using the table of physical constants and Debye temperature. ρ , C_V , E_0 , k , and calculated acoustic coupling constants (D_L & D_S) are presented in Table 2.

Table 2: Density (ρ : in 10^3 kg m^{-3}), specific heat per unit volume (C_V : in $10^6 \text{ Jm}^{-3}\text{K}^{-1}$), thermal energy density (E_0 : in 10^8 Jm^{-3}), thermal conductivity (k : in $\text{Wm}^{-1}\text{K}^{-1}$) and acoustic coupling constant (D_L , D_S) of Mg and MgZn_2 .

	ρ	C_V	E_0	k	D_L	D_S
Mg	1.74	1.592	2.91	15600	54.646	1.135
MgZn_2	5.48	0.846	1.789	4620	53.838	1.117

The calculated orientation dependent ultrasonic wave velocities and Debye average velocities at 300 K are shown in Figs. 1–4. Figs. 1–3 show that the velocities V_L and V_{S1} have minima and maxima, respectively, at 45° with the unique axis of the crystal while V_{S2} increases with the angle from the unique axis. The combined effect of SOEC and density is the reason for abnormal behavior of angle dependent velocities.

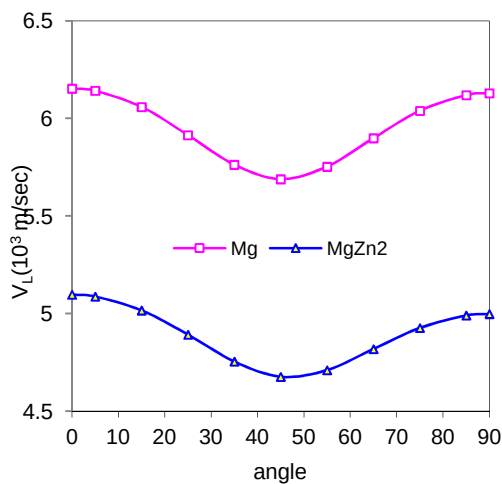


Fig.1: V_L vs angle with unique axis of crystal.

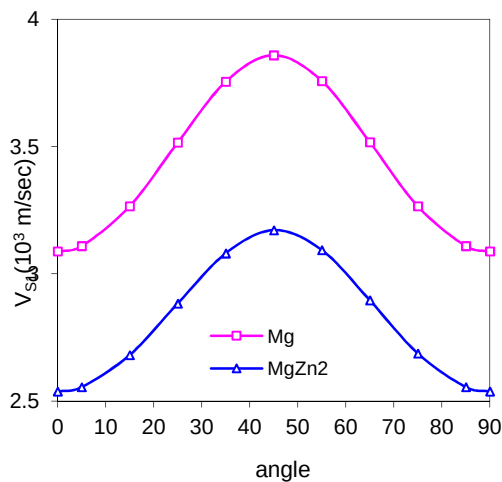


Fig.2: V_{S1} vs angle with unique axis of crystal.

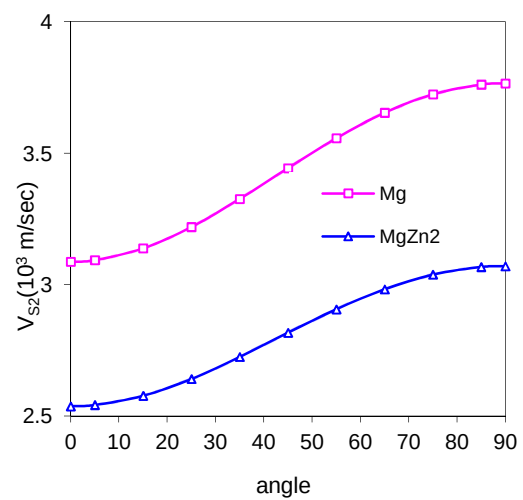


Fig.3: V_{S2} vs angle with unique axis of crystal.

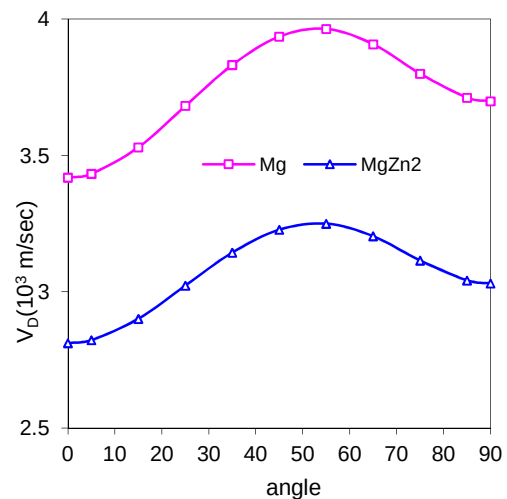


Fig.4: V_D vs angle with unique axis of crystal.

The nature of the angle dependent velocity curves in the present work is found to be similar as that for heavy rare-earth metals, laves-phase compounds, lanthanides metals and other

hexagonal structured materials [28-32]. Thus, the computed velocities for these compounds are justified.

Debye average velocities (V_D) of these materials are increasing with the angle and have maxima at 55° at 300 K (Fig. 4). Since V_D is calculated using V_L , V_{S1} and V_{S2} [17,22], therefore the angle variation of V_D is influenced by the constituent ultrasonic velocities. The maximum V_D at 55° is due to a significant increase in longitudinal and pure shear (V_{S2}) wave velocities and a decrease in quasi-shear (V_{S1}) wave velocity. Thus, it can be concluded that when a sound wave travels at 55° with the unique axis of these compounds then the average sound wave velocity is maximum.

The calculated thermal relaxation time is visualized in Fig. 5. The angle dependent thermal relaxation time curves follow the reciprocal nature of V_D as $\tau \propto 3K/C_V V_D^2$. This implies that τ for these are mainly affected by the thermal conductivity and specific heat per unit volume. The value of τ for hexagonal structured materials is the order of picoseconds [26]. Hence the calculated τ justifies the hcp structure of chosen metal and its alloy at room temperature. The minimum τ for wave propagation along $\theta = 55^\circ$ implies that the re-establishment time for the equilibrium distribution of thermal phonons will be minimum for propagation of wave along this direction.

Thus the present average sound velocity directly correlates with the Debye temperature, specific heat and thermal energy density of these materials.

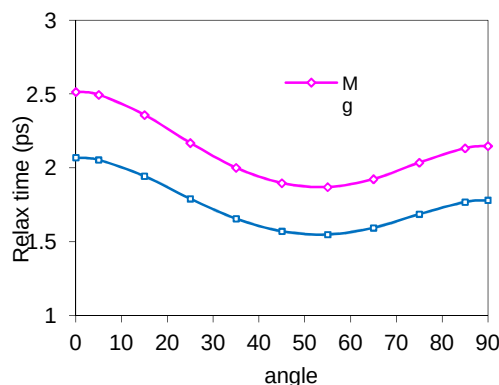


Fig.5: Relaxation time vs angle with unique axis of crystal.

3.3. Ultrasonic attenuation

In the evaluation of ultrasonic attenuation, it is supposed that wave is propagating along the unique axis ($<001>$ direction) of these materials. The attenuation coefficient over frequency square $(A/f^2)_{Akh}$ for longitudinal $(A/f^2)_L$ and shear wave $(A/f^2)_S$ are calculated using Eqn. (4) under the condition $\omega\tau \ll 1$ at room temperature. The thermo-elastic loss over frequency square $(A/f^2)_{Th}$ is calculated with Eqn. (5). The values of $(A/f^2)_L$, $(A/f^2)_S$, $(A/f^2)_{Th}$, and total attenuation $(A/f^2)_{Total}$ are presented in Table 3.

Table 3: Values of ultrasonic attenuation coefficients (in $10^{-15} \text{ Nps}^2 \text{ m}^{-1}$) of Mg and MgZn_2 .

	Mg	MgZn_2
$(A/f^2)_{Th}$	2.90	0.032
$(A/f^2)_L$	259.71	72.23
$(A/f^2)_S$	21.34	6.965
$(A/f^2)_{Total}$	283.96	79.23

Table 3 indicates that the thermo-elastic loss is very small in comparison to Akhieser loss and ultrasonic attenuation for longitudinal wave $(A/f^2)_L$ is greater than that of shear wave $(A/f^2)_S$. This reveals that ultrasonic attenuation due to phonon-phonon interaction along longitudinal wave is governing factor for total attenuation ($(A/f^2)_{Total} = (A/f^2)_{Th} + (A/f^2)_L + (A/f^2)_S$). The total attenuation is mainly affected by the thermal energy density and thermal conductivity. Thus, it may predict that at room temperature, MgZn_2 behaves as its purest form and is more ductile as evinced by minimum attenuation, while Mg is least ductile. Therefore, impurity will be least in the MgZn_2 at room temperature.

4. Conclusions

Based on the above discussion it is worthwhile to state that:

- Present method to evaluate second and third order elastic constants involving much body interaction potential for hexagonal structured metal and its alloy are correct.
- All elastic constants and density are mainly the affecting factors for anomalous behavior of ultrasonic velocity in these materials.
- The order of thermal relaxation time for these compounds found to be in picoseconds, which justifies their hexagonal structure at room temperature. The re-establishment time for the

equilibrium distribution of thermal phonons will be the minimum for the wave propagation along $\theta = 55^\circ$ due to being smallest value of τ along this direction.

- The ultrasonic attenuation due to phonon-phonon interaction mechanism is predominant over total attenuation as a governing factor thermal conductivity.
- The mechanical and ultrasonic properties (yield strength, ductility, elastic properties etc.) of MgZn_2 will be better than Mg due to their low ultrasonic attenuation.

The acoustic behavior in magnesium and Mg-Zn alloy as discussed above shows important micro-structural characteristic features, which are well connected to thermo-electric properties of the materials.

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