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## Elastic and acoustic properties of nanocrystalline Ni and Mg-doped hexagonal close-packed Ni nanoparticles

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### ABSTRACT

The ultrasonic properties like ultrasonic sound velocity in the hexagonal closed packed (hcp) nanocrystalline Ni and Mg-doped hcp Ni nanoparticles have been studied along unique axis at room temperature. The second- and third order elastic constants (SOEC & TOEC) have been calculated for these nanoparticles using Lennard–Jones potential. The velocities  $V_L$  and  $V_{S1}$  have maxima and minima respectively with  $45^\circ$  with unique axis of the crystal, while  $V_{S2}$  increases with the angle from unique axis. The inconsistent behaviour of angle dependent velocities is associated to the action of second order elastic constants. Debye average sound velocities of these nanomaterials are increasing with the angle and has maximum at  $55^\circ$  with unique axis at room temperature. Hence when a sound wave travels at  $55^\circ$  with unique axis of these nanomaterials, then the average sound velocity is found to be maximum. The comparison of calculated ultrasonic parameters with available theoretical/experimental physical parameters gives information about classification of these nanomaterials.

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### KEYWORDS

Nanoparticles;  
Elastic properties;  
Ultrasonic properties.

### INTRODUCTION

Ultrasonic offer the possibility to detect and characterize microstructural properties as well as flaws in nanomaterials, controlling materials behaviour based on physical mechanism to predict future performance of the nanomaterials. Various investigators have shown considerable interest on ultrasonic properties of different materials. Wave propagation velocity is 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  $\rho$  is the density of 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<sup>[1,2]</sup>. The elastic constants provide valuable information about the bonding characteristic between adjacent atomic planes and the anisotropic character of the bonding and structural stability<sup>[3,4]</sup>.

In recent years, nanoparticles of ferromagnetic metals Fe, Co and Ni attract more and more interests

**TABLE 1 : Second and third order elastic constants (SOEC and TOEC) & Bulk Modulus (B) in the unit of  $10^{10}\text{Nm}^{-2}$  of Ni and Ni: Mg (Mg-doped hcp Ni nanoparticles) at room temperature**

	$C_{11}$	$C_{12}$	$C_{13}$	$C_{33}$	$C_{44}$	$C_{66}$	<b>B</b>
Ni:Mg	16.49	4.05	3.53	17.07	4.24	6.47	8.03
Ni	33.28	8.17	7.23	35.37	8.67	13.05	16.35
<sup>[14]</sup> Ni	31.8	13.9	22.8	37.6	15.7		

	$C_{111}$	$C_{112}$	$C_{113}$	$C_{123}$	$C_{133}$	$C_{344}$	$C_{144}$	$C_{155}$	$C_{222}$	$C_{333}$
Ni:Mg	-269.00	-42.65	-9.07	-11.52	-57.65	-54.05	-13.43	-8.95	-212.84	-217.53
Ni	-542.78	-86.06	-18.54	-23.57	-119.49	-112.02	-27.46	-18.30	-429.47	-456.92

in terms of their special physical properties and potential applications in catalysts, high density magnetic recording media, medical diagnostics, ferrofluids and biomedical fields<sup>[5,6]</sup>. Among these ferromagnetic metals, Ni nanoparticles were investigated owing to their potential application in magnetic sensors and memory devices<sup>[7-10]</sup>. Chinnasamy et al.<sup>[11]</sup> obtained a mixture of fcc and hcp Ni nanoparticles with dimensions of tens of nanometers by the reduction in trimethylene glycol under alkaline condition. Mg-doped Ni nanoparticles with the hexagonal closed-packed and face-centered cubic structure have been synthesized by Yang et al.<sup>[12]</sup> using sol-gel method sintered at different temperatures. The average particle size of the sample with hcp structure evaluated by Scherrer equation was about 6.0 nm.

The elastic properties of Fe, Co and Ni at high pressure change substantially and knowledge of their behaviour provide information on the stability of a system, on the propagation of sound waves, and on the elastic anisotropy<sup>[13]</sup>. Systematic ab initio calculations of lattice constants, elastic constants and magnetic moments of Fe, Co and Ni in bcc, fcc and hcp structure have been evaluated by Guo et al.<sup>[14]</sup>.

There are three types of acoustic mode lattice vibration: one longitudinal acoustic and two transverse acoustical for hexagonal and cubic structured materials<sup>[15,16]</sup>. Hence, there are three types of acoustic wave velocities for each direction of propagation of wave, which are well related to second order elastic constants. But elastic constants of Mg-doped Ni nanoparticles and all the three type of orientation dependent acoustic wave velocity of these nanomaterials are not reported in literature. Therefore, in this work we predict the ultrasonic properties of hexagonal structured nanocrystalline

Ni and Mg-doped Ni nanoparticles at room temperature. The higher order elastic constants and ultrasonic wave velocities for these nanoparticles for each direction of propagation of wave are calculated at room temperature. The calculated ultrasonic parameters are discussed with related thermophysical properties for the characterization of the chosen materials. The obtained results are analyzed in comparison to other hexagonal structured materials.

## THEORY

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

### 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, ... 6) is component of strain tensor. Equations (1) and (2) leads six second and ten third order elastic constants (SOEC and TOEC) for the hexagonal close packed structure materials<sup>[1,17]</sup>.

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

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

## Full Paper

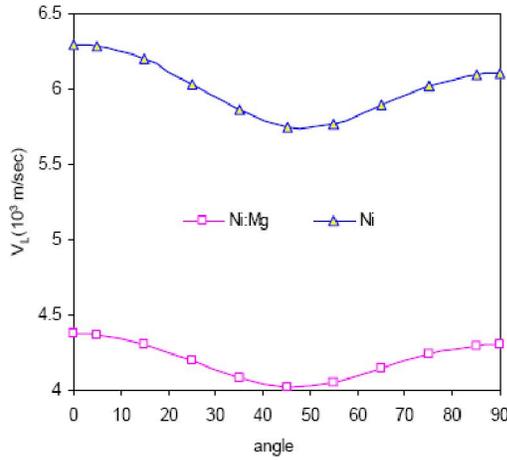


Figure 1 :  $V_L$  vs angle with unique axis of crystal

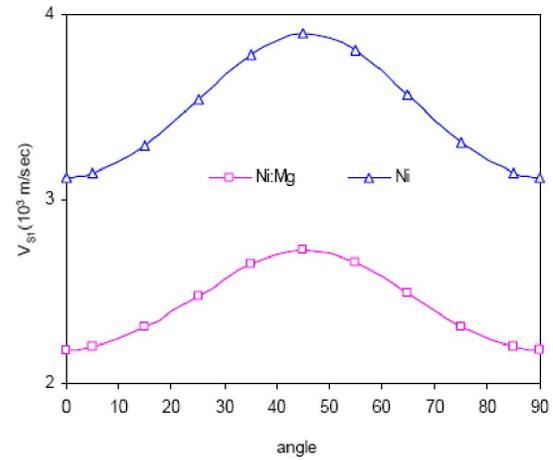


Figure 2 :  $V_{S1}$  vs angle with unique axis of crystal

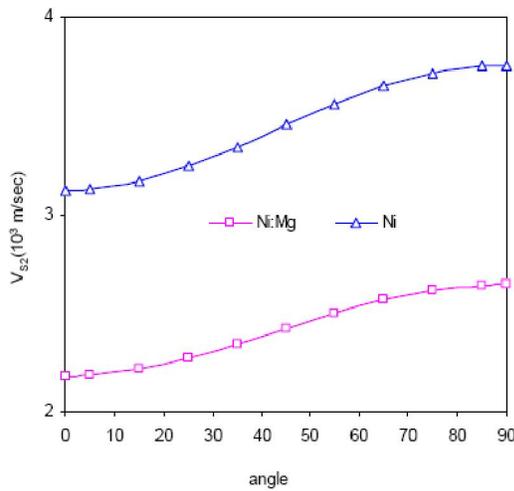


Figure 3 :  $V_{S2}$  vs angle with unique axis of crystal

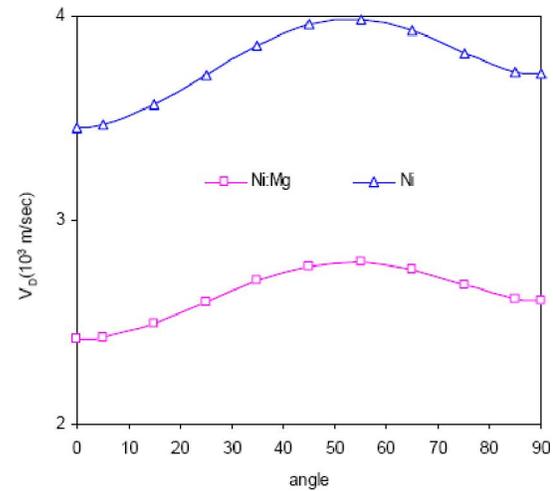


Figure 4 :  $V_D$  vs angle with unique axis of crystal

where  $p = c/a$ : axial ratio;  $C' = \chi a/p^5$ ;  $B = \psi a^3/p^3$ ;  $c = (1/8) \{ [nb_0(n-m)] / \{a^{n+4}\} \}$ ;  $\psi = -\chi / \{6a^2(m+n+6)\}$ ;  $m, n = \text{integer quantity}$ ;  $b_0 = \text{Lennard Jones parameter}$ .

### Acoustic wave velocity in hexagonal structured crystal

The anisotropic behavior of the material can be understood with the knowledge of ultrasonic velocity because the velocity is related to the second order elastic constants<sup>[18]</sup>. On the basis of mode of atomic vibration, there are three types of velocities (longitudinal, quasi shear and shear) in acoustical region<sup>[19]</sup>. These velocities vary with the direction of propagation of wave from the unique axis of hexagonal structured crystal<sup>[20]</sup>. The ultrasonic velocities as a function of angle between direction of propagation and unique axis for hexagonal structured materials are<sup>[21]</sup>:

$$V_L^2 = \{C_{33} \cos^2 \theta + C_{11} \sin^2 \theta + C_{44} + [C_{11} \sin^2 \theta - C_{33} \cos^2 \theta + C_{44} (\cos^2 \theta - \sin^2 \theta)]^2 + 4 \cos^2 \theta \sin^2 \theta (C_{13} + C_{44})^{1/2}\} / 2\rho \quad (4)$$

$$V_{S1}^2 = \{C_{33} \cos^2 \theta + C_{11} \sin^2 \theta + C_{44} - [C_{11} \sin^2 \theta - C_{33} \cos^2 \theta + C_{44} (\cos^2 \theta - \sin^2 \theta)] + 4 \cos^2 \theta \sin^2 \theta (C_{13} + C_{44})^{1/2}\} / 2\rho \quad (5)$$

$$V_{S2}^2 = \{C_{44} \cos^2 \theta + C_{66} \sin^2 \theta\} / \rho \quad (6)$$

where  $V_L$ ,  $V_{S1}$  and  $V_{S2}$  are longitudinal, quasi shear and pure shear wave ultrasonic velocities. Variables  $\rho$  and represent the density of the material and angle with the unique axis of the crystal respectively. The Debye temperature ( $T_D$ ) is an important physical parameter for the characterization of materials, which is well related to the Debye average velocity ( $V_D$ ).

$$T_D = \frac{\hbar V_D (6 \pi^2 n_a)^{1/3}}{K_B} \quad (7)$$

$$\text{here, } V_D = \left\{ \frac{1}{3} \left( \frac{1}{V_L^3} + \frac{1}{V_{S1}^3} + \frac{1}{V_{S2}^3} \right) \right\}^{-1/3} \quad (8)$$

where  $h$  is quantum of action and is equal to Planck's constant divided by  $2\pi$ ;  $K_B$  is Boltzmann Constant;  $n_a$  is atom concentration.

## RESULTS AND DISCUSSION

### Higher order elastic constants

The unit cell parameters 'a' (basal plane parameter) and 'p' (axial ratio) for Ni and Mg-doped hcp Ni nanoparticles (Ni:Mg= 0.95:0.05, in mol) are 2.47Å, 2.65Å and 1.649, 1.638 respectively<sup>[12,14]</sup>. The value of  $m$  and  $n$  for chosen nanomaterials are 6 and 7. The value of  $b_0$  is  $2.2 \times 10^{-65}$  erg  $\text{cm}^7$  for these nanoparticles. The SOEC and TOEC have been calculated for these nanoparticles using equation (3) and are presented in TABLE 1.

The calculated SOEC of Ni is smaller than the theoretical<sup>[14]</sup>. Actually Guo et al.<sup>[14]</sup> has based ab-initio local spin-density functional theory with generalized gradient corrections (GGA) approached to evaluate elastic constants, which is quite different from present approach. Although obtained SOEC are of the same order as others<sup>[14]</sup>. Relative magnitude of  $C_{11}$ ,  $C_{33}$ ,  $C_{12}$  are well presented by our theoretical approach. Which are in good agreement with 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 studies of other materials<sup>[1,19-22]</sup>. Hence our theoretical approach to evaluate elastic constants seems to valid for these nanoparticles. The bulk modulus (B) for these materials can be calculated with the formula  $B = 2(C_{11} + C_{12} + 2C_{13} + C_{33}/2)/9$ . The evaluated B for these nanomaterials is presented in TABLE 1.

### Ultrasonic velocity and allied parameters

The computed orientation dependent ultrasonic wave velocities and Debye average velocities at 300 K are shown in figure 1-4. Figure 1-3 show that the velocities  $V_L$  and  $V_{S1}$  have minima and maxima respectively at  $45^\circ$  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 reason for abnor-

mal behaviour of angle dependent velocities.

The nature of the angle dependent velocity curves in the present work is found similar as that for heavy rare-earth metals, third group nitrides, laves-phase compounds and other hexagonal wurtzite structured materials<sup>[16,19-22]</sup>. The chosen nanomaterials have shown similar properties with their crystal structure. Thus the angle dependencies of the velocities in these materials are justified.

Figure 1-3 indicate the magnitude of acoustic velocity, which is larger for Ni and smaller for Ni:Mg. The respective smaller magnitude of acoustical velocity in Ni:Mg is due to its lower elastic constants.

Debye average velocity ( $V_D$ ) of these nanomaterials is increasing with the angle and has maxima at  $55^\circ$  at 300 K (Figure 4). Since  $V_D$  is calculated using  $V_L$ ,  $V_{S1}$  and  $V_{S2}$ <sup>[16,17]</sup>, therefore the angle variation of  $V_D$  is influenced by the constituent ultrasonic velocities. The maximum  $V_D$  at  $55^\circ$  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  $55^\circ$  with the unique axis of these crystals then the average sound wave velocity is maximum.

The Debye average velocity for Ni and Ni:Mg is  $3.457 \times 10^3$  m/s and  $2.418 \times 10^3$  m/s respectively, which has a similar trend as the Debye temperature, because Debye temperature of Ni and Ni:Mg are  $591^\circ\text{K}$  and  $420^\circ\text{K}$  respectively<sup>[18]</sup>. The value of specific heat per unit volume ( $C_v$ ), thermal energy density ( $E_0$ ) of Ni and Ni:Mg are evaluated using tables of physical constants and Debye temperature, which are  $4.2 \times 10^6 \text{Jm}^{-3}\text{K}^{-1}$ ,  $3.6 \times 10^6 \text{Jm}^{-3}\text{K}^{-1}$  and  $7.86 \times 10^8 \text{Jm}^{-3}$ ,  $6.82 \times 10^8 \text{Jm}^{-3}$  respectively. Thus the preset average sound velocity directly correlates with the Debye temperature, specific heat and thermal energy density of these nanomaterials. The Debye average velocity has a minimum value for Ni:Mg in comparison to Ni along every direction of propagation (Figure 4). This indicates that Ni is much stable than Ni:Mg due to the large average sound velocity<sup>[21]</sup>.

## CONCLUSIONS

On the basis of above discussion, we conclude following points:

## Full Paper

- Our theory of higher order elastic constants is justified for the hexagonal structured nanomaterials.
- Although, the nature of angle dependency of acoustical velocity in these nanoparticles is quite similar to that of laves phase compounds, third group nitrides and other hexagonal materials but they favour instability due to lower anisotropy.
- All elastic constants are mainly the affecting factor for anomalous behaviour of acoustical velocity in these nanomaterials.
- The average sound velocity is a direct consequence of Debye temperature, specific heat and thermal energy density of these compounds.
- The mechanical properties of Ni are better than those of Ni:Mg, because Ni:Mg has low ultrasonic velocities.

Thus obtained results in the present work can be used for further investigations, general and industrial applications. Our theoretical approach is valid for ultrasonic characterization of these compounds at room temperature. The acoustic behavior in these nanomaterials as discussed above shows important microstructural characteristic feature, which are well connected to thermoelectric properties of the materials. These results, together with other well-known physical properties, may expand future prospects for the application and study of these nanoparticles. Also, the preliminary results obtained in this work can be used for further experimental investigation with pulse echo overlap (PEO) technique for ultrasonic measurements and with conventional analytic techniques such as polarizing microscopy, X-ray diffraction (XRD), surface tension, solid state nuclear magnetic resonance (NMR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

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