



Thermophysical and Ultrasonic Properties on Magnesium Oxide

U C Srivastava, S P Singh

Abstract: In present manuscript phonon dynamics of alkaline-earth oxides, MgO by including the three-body interconnections in the framework of 'van der Waals three-body force shell model' (VTBFSM) is based on my thorough theoretical study of the relevant research papers on this topic. The studies of lattice energy and other properties made by Huggins and Sakamoto [1]. The instigate work of Kellerman [2] for lattice dynamics of the alkali halides has provided attentive theoretically as well as experimentally. The thermal properties, densities of states (DOS), structure analysis, direction-dependent ultrasonic velocities and Debye velocity of magnesium oxide have been evaluated in present investigation. However, a considerable improvement in computational results has been obtained by the use of the present model and successfully predicted the lattice dynamic of MgO for the study of bulk thermo-elastic properties. The results of this investigation are discussed successfully with available experimental data.

Keywords : Phonon, Thermodynamic properties, Density of state, Ultrasonic velocity.

I. INTRODUCTION

Due to high-temperature applications of magnesium oxide (MgO), is a solid of great interest crystallize in NaCl-structures. In recent past, the availability of the phonon dispersion relations for MgO using the inelastic scattering of thermal neutrons has stimulated considerable interest in the study of its lattice dynamics among both theoretical and experimental workers. Theory of ionic solids by Lowdin's [3] and Lundqvist's [4] leads to a (MBF). No reports have been found of thermal and ultrasonic studies of the rock-salt structure. Lattice dynamic is one of the methods by the help of it the complete structural properties can be analyzed. The van der Waals interaction (VWI) potential owes its origin to the correlations of the electron motions in different atoms. Thus, the inclusion of VWI and TBI effects in RSM has utilized in Hitler-London and the free-electron approximations which is a significant advance over previous lattice models. The interaction systems of the present model thus consist of the long-range screened Coulomb, VWI, TBI and the short-range

overlap repulsion operative up to the second-neighbor ions. The crystal structure of MgO is illustrated in Fig.1

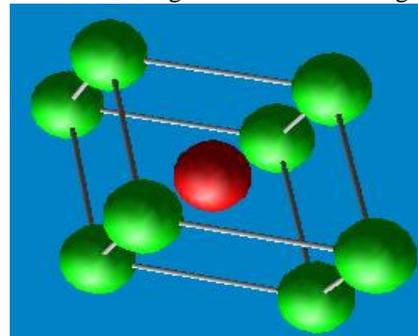
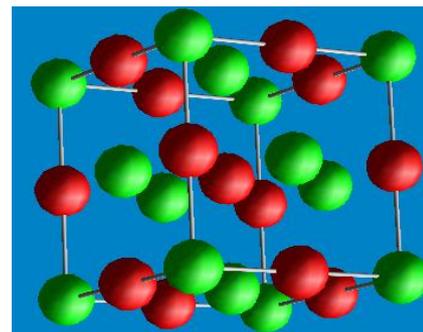


Fig 1.(a) Primitive unit cell Structure of MgO



(b) Crystallographic unit cell of MgO

II. THEORETICAL APPROACH

The concept of ionic interaction, van der Waals bonding, and covalente bonding can be understood easily on the atomistic approach model. The electrostatic or Coulombic energy term is the most important component in ionic or semi -ionic solids. Dick and Over Hauser [5] and Woods et al [6] has been

proposed (RSM) and it successfully applied to study of lattice property, effective up to the second neighbor in short-range interactions. The lattice vibrations are quantized in the solid phase and described by quasi-particles. Therefore, for the study of the complete dynamical behaviour of MgO has reported by introducing (VWI) effect & expression for the contribution of (TBI) that prove the relevance of use model (VTBFSM), which has been rigorously derived and exactly evaluated in the framework of RSM [7]. The relevant expression and general formalism of VTBFSM model given as

$$\Phi = \Phi^C + \Phi^R + \Phi^{TBI} + \Phi^{VW} \quad (1)$$

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Where Φ^C is a long-range Coulomb interaction potential. Thus, the total Coulomb energy of the crystal is

$$\Phi^C(r) = \sum_j \Phi^C \alpha_m \frac{Z^2 e^2}{r_0} (r_{ij})$$

Where α_m is the modelung constant and r_0 is intermolecular distance and Φ^or is repulsion potential. As a natural consequence of the anti-symmetry requirement on the wave function [8], this alteration in the electronic charge density causes a charge depletion. This interaction potential is expressed as

$$\Phi^{TBI} = \alpha_m \frac{Z^2 e^2}{r_0} \left[\frac{2n}{Z} f(r)_0 \right] \quad (2)$$

Where, the term $f(r)_0$ is electron wave-functions. The introduction of VWI and TBI in the framework of RSM leads to the secular determinant:

$$|D(\vec{q}) - \omega^2 \underline{M} I| = 0 \quad (3)$$

Here $\underline{D}(\vec{q})$ is the (6 x 6) dynamical matrix for the Rigid Shell model expressed as:

$$\underline{D}(\vec{q}) = (\underline{R}' + \underline{Z}_m \underline{C}' \underline{Z}_m) - (\underline{T} + \underline{Z}_m \underline{C}' \underline{Y}_m) \times (\underline{S} + \underline{K} + \underline{Y}_m \underline{C}' \underline{Y}_m)^{-1} (\underline{T}^T + \underline{Y}_m \underline{C}' \underline{Z}_m) \quad (4)$$

where $\underline{R} = \underline{T} = \underline{S} \underline{C}'$ is modified long-range interaction matrix have been given by Verma and Singh [7].

$$\underline{C}' = \underline{C} + (\underline{Z}_m^{-2} \underline{Z}_m f_0') \underline{V} \quad (5)$$

Where f_0' is the first -order space derivative and \underline{Z}_m modified ionic polarizability. The second neighbor dipole-dipole (VWI) energy, is expressed as:

$$\Phi_{dd}^{vwi}(r) = -S_v \left| \frac{C_{++} + C_{--}}{6r^6} \right| = \Phi^v(r) \quad (6)$$

Where, S_v is lattice sum of positive-positive and negative-negative ion pairs C_{++} and C_{--}

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2.1 Thermodynamically properties

Density of state, temperature dependence of free energy, specific heat capacity at constant volume were calculated. The C_v was calculated using the following equation [9-10].

$$U = \int_0^{v_m} \frac{h\nu^3}{e^{h\nu/kT} - 1} d\nu \quad (7)$$

$$\text{and } C_v = 3NK_B \frac{\sum_{\nu} \{E(x)\} G(\nu) d\nu}{\sum_{\nu} G(\nu) d\nu} \quad (8)$$

Where $E(x)$ is the Einstein function defined as

$$E(x) = x^2 \frac{e^{(x)}}{\{e^{(x)} - 1\}^2} \quad \text{and } \sum_{\nu} G(\nu) d\nu = \text{Total number of frequencies considered lying in frequency interval.}$$

According to thermodynamics, the equilibrium of a solid at a temperature T is determined by the minimum value of the free energy.

$$F = U - TS \quad (9)$$

2.2. Density of states

To determine the phonon (DOS) for each polarization is given by VTBF model.

$$g(\omega) = \frac{dN}{d\omega} = N \int_{BZ} \sum_j \delta[\omega - \omega_j(q)] dq = \left(\frac{VK^2}{2\pi^2} \right) \left(\frac{dK}{d\omega} \right) \quad (10)$$

$N = (L/2\pi)^3 (4\pi K^3/3)$, K is wave vector and $L^3 = V$. Where N as a normalization constant such that $\int g(\omega) d\omega = 1$ and $g(\omega) d\omega$ is the ratio of the number of eigen states in the frequency interval.

2.3. Ultrasonic velocities

The propagation of ultrasonic waves through anisotropic solids depends on the strains along the <100>, <110>, <111> directions. When the ultrasonic waves propagate through a medium, their velocity has three modes of propagation, one longitudinal acoustical (V_L) and two shear acoustical (V_{S1} , V_{S2}). The expressions for V_L , V_{S1} and V_{S2} are given in literature [11,12].

III. RESULTS AND DISCUSSION

The effect of pressure on the crystal structure, electronic structure and vibrational properties have been computed in present study. The input data and the model parameters of MgO reported in table -1 and 2 and Orientation dependent ultrasonic velocities & Debye velocity in table-3 taking the values of input constants from [27-28] and calculated the model parameter. Ultrasonic velocity plays a significant role in the material characterization. The propagation of ultrasonic waves through anisotropic solids depends on the strains along the <100>, <110>, <111> directions. The Internal energy, entropy, free energy heat capacity and dispersion relation curve at temperature 500K has shown in Fig.2-6 with the available theoretical and experimental result which has shown parallel to the present calculated results.

Table 1 Input data for MgO in terms of C_{11}, C_{12}, C_{44} in ($10^{11} \text{ dyn cm}^{-2}$), r_0 (10^{-8} cm), $\epsilon_0, \epsilon_\infty, \nu_L$ (THz) and ν_T (THz).

Input Data	Expt[19]	Expt[20]
C_{11}	30.70[9]	28.917[15]
C_{12}	8.50[9]	8.796[15]
C_{44}	15.89[9]	15.461[15]
r_0	4.213[9]	2.106[16]
ϵ_0	9.86[10]	9.86[10]
ϵ_∞	2.957[17]	2.956[10]

v_L	21.55[17]	21.679[18]
v_T	11.81[14]	11.870[10]

Table 2 Calculated Model Parameters by using values Ref [19,20]

Parameter Values	Expt[19]	Expt[20]
Z_m	2.00	2.00
$r_o f_o'$	-0.330	-0.152

A	31.319	7.912
B	-3.9431	-1.350
d_1	-0.1371	-0.0962
d_2	-0.5977	-0.732
Y_1	1.6441	0.350
Y_2	-3.443	-3.334

Table.3 Orientation dependent ultrasonic velocities V_L, V_{S1}, V_{S2} and V_D (in 10^3ms^{-1}) of MgO at room temperature calculate using values uses from [19,20]

Material Orientation	V_L		V_{S1}		V_{S2}		V_D		
	Ref[19]	Ref[20]	Ref[19]	Ref[20]	Ref[19]	Ref[20]	Ref[19]	Ref[20]	
MgO	<100>	0.9260	0.8986	2.1067	2.1067	2.1067	2.0781	0.7889	0.8096
	<110>	3.1485	3.0961	2.1067	2.4902	2.4902	2.0781	0.7813	0.8102
	<111>	3.2186	3.1762	1.8832	1.8832	1.8832	1.8201	0.7889	0.8096

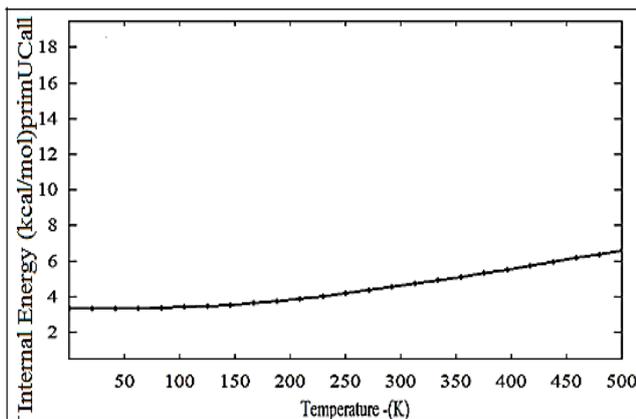


Fig. 2 Internal Energy of MgO

internal energy value has started from 2 (kcal/mole) prime unit cell at 0 K and 18 (kcal/mole) prime unit cell at the temperature of 500K. So the internal energy value increased constantly at 150K and then the internal energy sharply

increasing for the above temperature range up to 500 K.

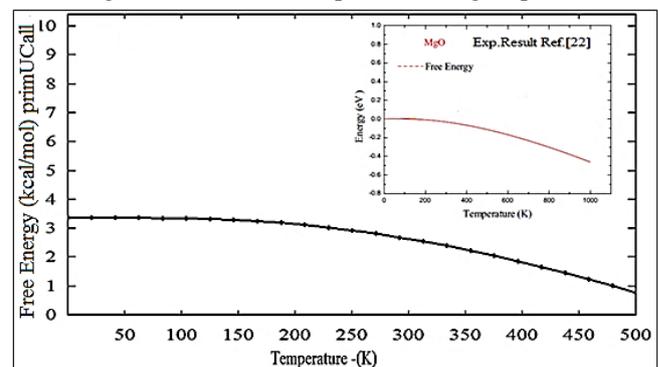


Fig.- 3 Free Energy curve of MgO

On raising the temperature free energy value of MgO is continuously decreasing with increasing temperature. In fig-3. on raising the temperature up to 150K free energy value continuously increasing and then further energy transforms reversibly decreases continuously up to 500K at high temperature energy dissipation more rapidly can be seen. our theoretical reported result is agree well with experimentally reported result by ref.[22].

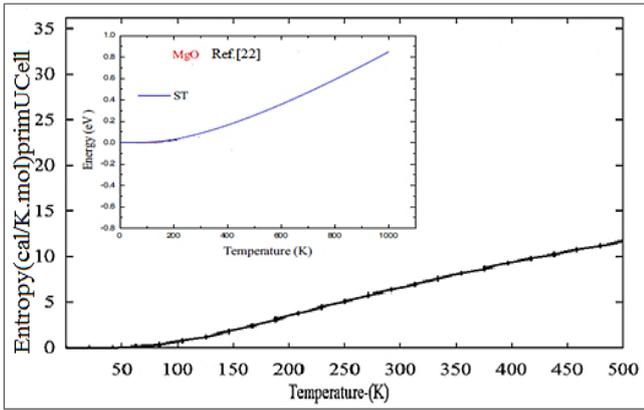


Fig.4 Entropy curve of MgO

plot of entropy versus temperature for MgO is shown in fig 4. Entropy value continuously increases up to 11 (cal/K.mol per unitcell) on the temperature of 500K. An abrupt change has been noted and sharply increases entropy from zero value to 500 K. At lower temperature disorder of crystal can be seen but for higher temperature more vibration in material occurred so ideal condition of entropy has been observed.

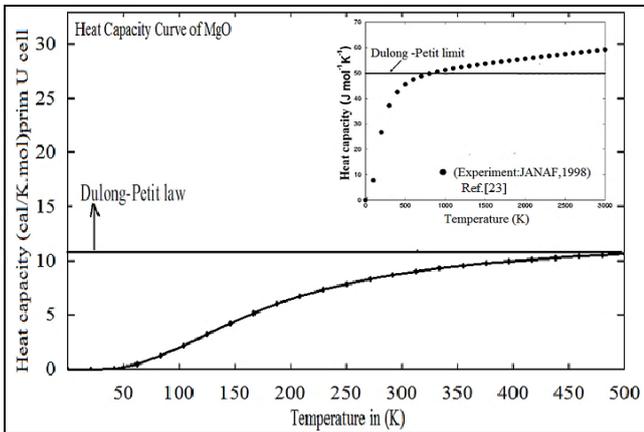


Fig.5 Heat Capacity curve of MgO

The heat capacity is raised continuously on increasing in temperature value from 0 to 7 (cal/ k .mole per unit cell) at the temperature range of 50K to 300K. The exponential increment in specific heat value curve has been observed the value from low-temperatures were smoothly growing on. At 300 K the heat capacity of MgO smoothly increases, but on the other higher value of temperature shown in fig. 5. Heat capacities increase very small and then remain constant for further increases in temperature value up to 500K. As the temperature increases the value of heat capacity increases and approaches a constant at high temperatures that tend to the Dulong-Petit limit [29]. However, at higher temperatures, the anharmonic effect on the heat capacity is very close to the Dulong-Petit limit. In fig .5 the experimental reported result is given by [25] and at a lower temperature less number of points available but their nature is similar to theoretical result.

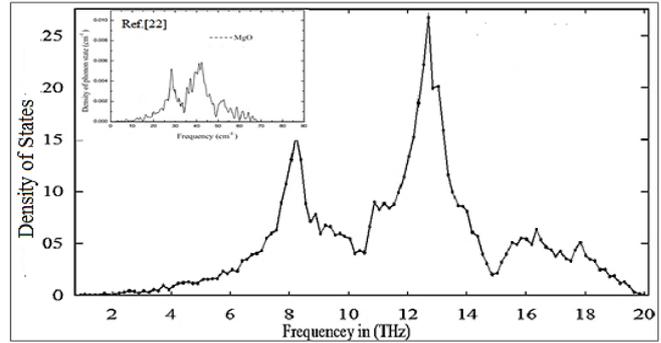


Fig.6 Density of states curve of MgO

The density of states (DOS) of a system describes the number of states per interval of energy at each energy level that is available to be occupied. The theoretical study of (DOS)of MgO is used as a reference and this theoretical finding is in qualitative agreement with the experimental observations. The DOS curve with frequency (THz) value is reported in fig .7. At frequency of 13 (Thz) the peak attended the maximum value, there are many states available for occupation and on increasing the frequency value a local density of states (LDS) available, frequency of 8 (Thz) more occupied states are available and less occupied states are above the 14 THz frequency range the gap has been observed after 15 (THz) again distortion in peaks can be seen. The illustrated thermodynamic properties obtained confirmed the characteristics of MgO. If compare to the experimental result the peak at 11 THz are similar to our theoretical result but above this value some sharp electronic peak available from 35 cm-1 to 45 cm-1 so in this range the discrepancy in spectroscopic experimental and lattice dynamical result occurred and rest value the result is approximately similar.

IV. CONCLUSION

The lattice dynamical calculations for alkaline-earth oxides MgO based on 11 parameters. Orientation dependent ultrasonic velocities is reported theoretically in table-3 by using the experimental data [19,20]. The uncertainty in the thermal expansion for MgO is seen that using the phonon theory do not converge for T>2000 K, whereas those by [30] show convergence up > 3000 K has been observed at high temperature but it does not affect the result. In the present study despite the lower symmetry of MgO the uncertainty as to the exact nature of the distortion of the lower-temperature structure. Our theoretical study at the lower temperature side shows a better agreement, but at the higher temperature side, slight disagreement may be ascribed to the non-inclusion of the harmonic interactions are using in present report, which justify the incorporation of (VWI) is essential. The Complete lattice dynamical, thermodynamical property and density of state curve of MgOtheoretically reported has agreed with different reported data [15-26].

The authors and more researchers have already used the present model and successfully reported the value of alkali halides and semiconductor materials [31-37].To sum up, we can say that the contributions of VWI and TBI are essential for the description of the lattice dynamics and thermodynamical study of MgO.



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