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Study of Elastic and Anharmonic Properties of Transition Metal Oxides

Surendra Kumar Singh
(TGT(Physics)Mother Teresa Senior Secondary Co-Ed School, Bhopal)

Abstract: *The theory of elastic constant is capable to explain the concept of Hook's law. According to this, a small amount of deformation in a solid is directly proportional to stress and the strain components are linear function of stress components. The ratio of stress to strain is known as the modulus of elasticity. The third and higher order terms are neglected in the case of harmonic approximation. Some derivations from Hook's law at small deformation has been reported by some physicists which is mainly due to the omission of higher order terms of the strain energy. This reason and derivation motivated the workers to focus their attention to Third Oreder Elastic Constants(TOECs). In our present study we shall deal and stick with Second Order Elastic Constants (SOECs), Third Order Elastic Constants (TOECs) and pressure derivatives of second order elastic constants by the theory of finite deformation.*

I. Introduction

There are various properties of solids which is not possible to explain with the help of harmonic interaction potential model itself. On the basis of harmonic theory of interaction following points can be concluded[1].

1. There is not any thermal expansion in solids.
2. Adiabatic and Isothermal elastic constants of the solids are equal.
3. The elastic constants of the solid does not depends on the pressure and temperature.
4. The heat capacity becomes constant at high pressure.
5. Two lattice waves do not interact with each other.
6. A single lattice wave does not decay or change its form with times.

After the study it has been found that not even a single consequence explained by harmonic theory is satisfied accurately in the real crystal. The deviations may attribute to the neglection of anharmonic(higher than quadratic) terms in the interatomic displacements. The anharmonic properties of solids helps us to know about the important information about their interatomic forces. The main properties among them are pressure derivative of Second Order Elastic Constants (SOECs).

Theory

The theory of elastic constant is capable to explain the concept of Hook's law. According to this, a small amount of deformation in a solid is directly proportional to stress and the strain components are linear function of stress components. The ratio of stress to strain is known as the modulus of elasticity. The third and higher order terms are neglected in the case of harmonic approximation. Some derivations from Hook's law at small deformation has been reported by some physicists which is mainly due to the omission of higher order terms of the strain energy. This reason and derivation motivated the workers to focus their attention to Third Oreder Elastic Constants (TOECs). In our present study we shall deal and stick with Second Order Elastic Constants (SOECs), Third Order Elastic Constants (TOECs) and pressure derivatives of second order elastic constants by the theory of finite deformation

We shall work on lattice theoretical study of the second and higher order elastic constants of the cubic crystals using the method of homogeneous finite deformation. It is clear that potential is independent of temperature T and entropy S, it means mechanical elastic constants depends only on configuration of the crystal. If vibration dependent terms are ignored, F =U then there is no distinction between the isothermal and adiabatic constants. M.Krishnamurthy and M. Suryanarayan [2] has conducted the survey regarding the application of ultrasonic waves for the study of the elastic properties of solids. An excellent reviews on this important branch of solid state physics have been previously published [3-5]. Earlier to this publication some other contemporary works reported an enormous progress [3-5] both experimentally and theoretically in the branch of crystal elasticity. There has been a continuous progress in the theory of elasticity up to now. Remarkable progress has been witnessed in the determination of elastic constants of crystal during recent years. The study of elastic properties of solids under varying pressure has also been assumed special significance because of the recent interest developed in the third order elasticity.

We have developed Three Body Potential Model (TBPM) to study the phase transition in transition metal oxides under high pressure. Further we have applied this model to describe the anharmonic properties of transition metal oxides. In this process, we have focused systematically on the study of third order constants, pressure derivative of second order elastic constants and behavior of second order elastic constant at different varying pressure. A large number of attempts [6-9] has been made to understand the anharmonic properties theoretically as well as experimentally. The anharmonic properties directly depends on higher than quadratic order elastic constants.

Third Order Elastic Constants has very great significance and importance in the field of study of phase transition and anharmonic properties of solid. They are dominant in higher derivatives of potential energy. Their interpretation involves anharmonic force constants derived in VVF (Valence Force Field) model [6,7,10]. In due course of time different experimental techniques [11-15] have been developed which enables us to measure the Third Order Elastic Constants (TOECs) more accurately. It can be calculated by propagating a sound wave of small amplitude in statically stretched media and measuring its velocity. The study of elastic properties of solids under varying pressure by M. Krishnamurthy and M. Suryanarayan is of great significance due to increased interest in the field of third order elasticity. Very precise measurement of velocity of ultrasonic wave is needed to understand the elasticity of crystal under varying environmental conditions.

II. Second Order Elastic Constants:-

We have calculated second order elastic constants (SOECs), C_{11},C_{12} and C_{44} of transition metal oxides and their pressure derivatives at 0°K. These second order elastic constants are the functions of first and second order derivatives of short range potential. These calculations provides adequate knowledge about the effect of short range forces on these materials. C_{11} represents a measure of resistance to deformation by a stress applies on (110) plane with polarization in the direction <100>, C_{44} represents the measure of resistance to deformation with respect to a shearing stress applied across the (100) plane with polarization in the <010> direction. The expression for Second Order Elastic Constants are given as follows:

$C_{11} = e^2/4r_0^4[-5.112z\{z + 12f(r)\} + A_1 + (A_2 + B_2)/2 + 9.320za''(r)]$ –(1)

$C_{12} = e^2/4r_0^4[0.226z\{z + 12f(r)\} - B_1 + (A_2 - 5B_2)/4 + 9.320zaf'(r)]$ ---(2)

$C_{44} = e^2/4r_0^4[2.556z\{z + 12f(r)\} + B_1 + (A_2 + 3B_2)/4]$ ---------(3)

In the above equations the symbol (A_1, B_1) and (A_2, B_2) are the short range parameters for the nearest neighbor (nn) and next nearest neighbor (nnn).

$A_1 = 8r_0^3/e^2[(b/\rho^2)\exp(r_1 + r_2 - r)/\rho]_{r = a}$ ----------------- (4)

$B_1 = 8r_0^3/e^2[(-b/\rho r)\exp(r_1 + r_2 - r)/\rho]r = a$ -----------------------------(5)

$A_2 = 16r_0^3/e^2[(b/\rho^2)\{(1.75)\exp^{(2r1-r/\rho)} + (0.25)e^{(2r2-r/\rho)}]_{r = \sqrt{2}a}$ –-----------(6)

$B_2 = 16r_0^2/e^2[(-b/\rho r)\{(1.75)\exp^{(2r1-r/\rho)} + (0.25)e^{(2r2-r/\rho)}]_{r= \sqrt{2}a}$ ---------(7)

$C_1 = A_1^2/B_1$ and $C_2 = A_2^2/B_2$ --(8)

Prressure Derivatives of Second Order Elastic Constants:-

Pressure derivatives can be obtained directly by differentiating the expression for Second Order Elastic Constant and using the equilibrium condition.

$dS/d\rho = -(2\Omega)^{-1}[23.682Z(Z + 12 f(r)_0) + C_1 + (C_2 + 6A_2 - 6B_2)/2 - 50.0752$

$Z(a\delta f/\delta r)_0 + 13.9808 Z (a^2\delta^2 f/\delta r^2)_0]$ ---------------(9).

$dK/d\rho = -(3\Omega)^{-1}[13.980Z(Z + 12 f(r)_0) + C_1 - 3A_1 + C_2 - 3A_2 - 167.7648 Z(a\delta f/\delta r)_0 + 41.9420 Z (a^2\delta^2 f/\delta r^2)_0]$-------------------------(10)

$dC_{44}/d\rho = -(\Omega)^{-1}[11.389Z(Z + 12 f(r)_0) + A_1 - 3B_1 + (C_2 + 2A_2 - 10B_2)/2$

$- 44.6528Z(a\delta f/\delta r)_0]$ -------------------------- (11).

Ω= -2.330 Z(Z + 12 f(r)$_0$) + A_1 + A_2 + 27.9612 + Z(aδf/δr)$_0$ + 8a^{4}P/e^2 -- (12).

Third Order Elastic Constants:-

The third order elastic constants are defined as the coefficient of the cubic term in the Taylor's series expansion for the strain energy of the crystal. As we have discussed that anharmonic terms are important and necessary to be included in the study. They also make significant contribution to the total energy of the solid. The detailed study of second order elastic constants, third order elastic constants and pressure derivatives of second order elastic constants are given in this chapter. Extensive work has been done for the study of the second order elasticity, and this work has also helped in the verification of existing theories of second order elasticity. However, practically no work has been done on third order elasticity and unless this is done, the existing theories of third order elasticity can not be verified.

We have incorporated the corrected expressions for third order elastic constants which was reported by Sharma [20] and have been successfully used in some earlier studies of zincblende compounds [18,19]. These expression have been derived from potential energy of solids [16,17] following the method of homogenous deformation [20]. The expression for Third Order Elastic Constants are given below:

$C_{111} = e^2/4a^4[\ 37.5626Z(Z + 12f(r)_0) + C_1 - 3A_1 + (C_2 - 3A_2 - 9B_2)/4 -$

$89.3040 + Z(a\delta f/\delta r)_0 + 13.9809\ Z\ (a^2\delta^2 f/\delta r^2)_0] - 3\rho$

$C_{112} = e^2/4a^4[\ -4.8358\ Z(Z + 12f(r)_0) + (C_2 - 3A_2 + 3B_2)/8 -$

$18.6400 + Z(a\delta f/\delta r)_0 + 4.6603\ Z\ (a^2\delta^2 f/\delta r^2)_0]$

$C_{123} = e^2/4a^4[\ 2.7172\ Z(Z + 12f(r)_0) + 16.6920\ Z(a\delta f/\delta r)_0\ ]$

$C_{144} = e^2/4a^4[\ 2.7172\ Z(Z + 12f(r)_0) + 5.5642\ Z(a\delta f/\delta r)_0\ ]$

$C_{166} = e^2/4a^4[\ -7.1658\ Z(Z + 12f(r)_0) - 2(B_1 + B_2) + (C_2 - 3A_2 + 3B_2)/8 +$
$5.5642\ Z(a\delta f/\delta r)_0] - 2\rho$
$C_{456} = e^2/4a^4[\ 1.5522\ Z(Z + 12f(r)_0) - (B_1 + B_2) - \rho]$

III. Result and Discussion.

In our model we have computed the elastic properties of materials under experiment. This helps us to test the mechanical stability of our model. Second Order Elastic Constants (SOECs) C_{11}, C_{12} and C_{44} exhibits the complete picture about the properties of any compounds. C_{11} helps us to measure resistance against deformation when stress is applies on (110) plane with polarization in direction <100>. C_{44} represents the measurement of resistance against deformation with shearing stress applied across the (100) plane with polarization in the <010> direction. We have calculated second order elastic constants (SOECs) and their combination $C_L = [\ C_{11} + C_{12} + 2C_{44}]/2$ and $C_S = [C_{11}-C_{12}]/2$. The results we got are at par with first order and describes the character of transition for transition metal compounds. As it was earlier reported, these are similar to the results of Calcium Chalcogenides which belongs to the same family of compounds of NaCl (B_1) structure. They also exhibits the similar type of transition from NaCl (B_1) to CsCl (B_2) structure.

After the study Vukcevich [22] has established that shear elastic constant C_{44} should be the value of non-zero in the case of stable phase of a crystal for the mechanical stability. For mechanical stability of a crystal, we relied on Born criterion according to which density of elastic energy must be a positive definite function of strain. For this criterion the eigen values of the elastic constant matrix should be positive. Thus on the basis of above criterion following expressions can be stated.
$(\ C_{11} + 2C_{12})/3 > 0$
$C_{44} > 0$
$C_S = (\ C_{11} - C_{12})/2 > 0$

Here C_{44} is tetragonal modulus and C_S is the shear modulus of a cubic crystal. The value of C_{44}/B_T and C_S/B_T at the phase transition pressure satisfy the conditions given in above equation. The estimated tetragonal modulus for TiO and TiN are 142 GPa and 179 GPa respectively.. The values of C_{11},C_{12} and C_{44} nearly agrees with the theoretical data and is better matching with experimental value. As there are no experimental data available for elastic constants of TiO, we were restricted to compare our results with the theoretical results of Ahuja et al [21].

On overall discussion it can be said that our present model is appropriate enough to study the elastic and anharmonic behaviour of transition metal oxides. Finally , it can be concluded that during the crystallographic phase transition from the structure of NaCl to CsCl the discontinuity in volume shows the same results as it was established by experimental and other theoretical techniques. We also have checked the criterion for mechanical stability of the crystal in terms of the elastic constants. Finally, on the basis of overall discussion and achievement we can claim that the Three Body Potential Model (TBPM) model is exactly appropriate to describe the phase transition and elastic behavior under high pressure in transition metal oxides.

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