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RESEARCH PAPER

Grüneisen Parameter Variation Consideration in Theoretical High-Pressure Studies for C_{60}

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Abstract

Grüneisen approximation was used for evaluating effect of high pressure on phonon frequency spectrum and phonon density of states of solid fullerene. Two equations of state (EOS), Sharma and Kumar EOS and Birch–Murnaghan EOS, were used to calculate the variation of volume compression ratio under high compression. Obtained results were compared with published experimental data. C_{60} phonon frequency spectrum at ambient pressure, calculated in the literature, was implemented to use in the present work to demonstrate how it is affected under the influence of high pressure by using Grüneisen approximation and different EOSs, in comparison with published results for the effect of high pressure on intermolecular and intramolecular phonons in solid C_{60}. The achieved results revealed the importance of considering pressure dependence of first Grüneisen parameter (γ) and second Grüneisen parameter (q), in theoretical high-pressure studies of C_{60}.

Keywords Equation of state (EOS) · C_{60} · High pressure P · First Grüneisen parameter · Phonon density of state

1 Introduction

Solid fullerene C_{60} has face-centered cubic structure, at room temperature. It undergoes phase transition at high temperature and high pressure. Many physical properties as well as structural stabilities of $_{C60}$ are strongly affected by application of high pressure (Schober and Renker 1999; Adnan et al. 2020). Thermoelastic properties of this crystal have become a subject of numerous of studies (Duclos et al. 1991; Sharma et al. 2010). Present work focuses on understanding variation of Grüneisen parameter and its influence on phonon frequency spectrum of C_{60} under high pressure. However, Grüneisen parameter describes the effect of changing volume of solid matter on vibrational motions of atoms. Thus, the variation of Grüneisen parameter under high pressure leads phonon frequency spectrum volume dependent. Hence, Grüneisen parameter particularly its volume dependence is profound in the field of thermoelastic properties of solids. Many researchers (Dixit and Shanker 1995; Xing et al. 2008; Sirwan and Adnan 2014) have formulated variation of Grüneisen parameter under high pressure. These formulations were used in the current work to investigate the effect of Grüneisen parameter variation under high pressure on evaluation of C_{60} phonon frequency spectrum. Based on interatomic potentials, various properties of C_{60} such as bulk modulus and lattice parameter at atmospheric pressure have been investigated (Jindal et al. 2000). Variation of bulk modulus and spinodal pressure of C_{60} have been investigated by using different EOSs (Adnan et al. 2020). Its specific heat capacity and bulk modulus under high pressure calculated based on generalized free-volume theory (Yu et al. 1993a). Moreover, phonon frequency spectrum of C_{60} at ambient condition has been determined experimentally using inelastic neutron scattering (Yu et al. 1993b) along with theoretical evaluation. C_{60} phonon frequency spectrum and Debye temperature under strong compression has been investigated (Adnan et al. 2022). Sun et al. (2006) used intermolecular and intramolecular potential model to calculate the phonon dispersion and phonon frequency spectrum at

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various pressure ranges. By using Grüneisen approximation theory in the present frame of work, the theoretically calculated phonon frequency spectrum at atmospheric pressure (Yu et al. 1993b) is used to find how density of states and frequencies of the modes change under the application of high pressure. First Grüneisen parameter (γ) also depends on the second Grüneisen parameter (q), which is also assumed to be pressure dependent. A nanomaterial equation of state (S-K EOS) (Sharma and Kumar 2010) and B-M EOS (Birch 1947) are used in the present calculations to demonstrate their validity to be applied on C_{60}. The results of the studies of phonon frequency spectrum will be compared with evaluated data by the model of (Yu et al. 1993a) and an adequate agreement could be observed, which reveal the importance of considering γ and q parameters variations in evaluation C_{60} phonon frequency spectrum under high pressure.

2 Method of the Study

Study of fundamental properties of condensed matter under high pressure and high temperature is normally performed with equations of state. Varieties of equations of state have been derived in literature (Birch 1947; Vocadlo et al. 2000; Sirwan and Adnan 2014) and each of them was formulated based on different considerations. Most equations of state give nearly similar results over low-pressure ranges. However, as the pressure rises the results of different EOSs exhibit more divergence. One of the most popular equations of state (EOS) which has been intensively used by many researchers is Birch–Murnaghan EOS (Siham et al. 2022). It is derived based on the finite strain model in solids. B-M EOS is given in Eq. 1 in the following. (Birch 1947):

$$P_{B-M} = \frac{3K_0}{2}\left(\eta^{-7/3}-\eta^{-5/3}\right)\left(1+\frac{3}{4}\left(K'_o-4\right)\left(\eta^{-2/3}-1\right)\right) \quad (1)$$

where P_{B-M} : pressure due to Birch–Murnaghan equation of state EOS, K_0 : bulk modulus at ambient pressure, K'_0 : first pressure derivative of bulk modulus, and $\eta = \frac{V_p}{V_0}$: volume compression ratio. V_p and V_0 are volume at high pressure and atmospheric pressure, respectively.

Another equation of state which is used in the present work is a new isothermal equation of state derived on the basis of nano-size consideration to apply on nanomaterials, and given in Eq. 2 (Sharma et al. 2010):

$$P_{S-K} = K_0(1-\eta) + \frac{1}{2}K_0(K'_0+1)(1-\eta)^2 \quad (2)$$

where P_{S-K}: pressure due to Sharma and Kumar EOS. Equations 1 and 2 are combined, in this work with the Grüneisen approximation to study phonon frequency spectrum of solid C_{60} under high pressure.

2.1 Lattice Vibrations and Phonons

The vibrational motion of atoms in solid phase is represented as quantized energy in the form of phonons. According to the Debye theory in specific heat capacity, a wide range of frequencies ω (modes) presents in the crystal. Hence, the number of modes in the range of frequency ω to ω + dω is called density of state g(ω). In the Grüneisen approximation theory (Vocadlo et al. 2000), vibrational frequencies of individual atoms in a solid vary with the volume V, shown in Eq. 3:

$$\gamma_i = -\frac{\partial \ln \omega_i}{\partial \ln V} \quad (3)$$

where γi: Grüneisen parameter for the i^{th} mode and ω_i: frequency of the i^{th} mode of vibration.

Equation (3) shows that the vibrational frequency of atoms depends on the lattice volume that can be altered with the application of high pressure.

Grüneisen parameter represents a very important concept in solid-state matter, for its influence on density of modes of vibrational motions in crystals.

2.2 Pressure Dependence of Grüneisen Parameter and Lattice Vibrations

Anharmonic property of solid leads the Grüneisen parameter pressure dependent. Therefore, an expression of the volume dependence of the Grüneisen parameter is written in Eq. 4 (Boehler and Ramakrishnan, 1980):

$$\gamma_p = \gamma_o(\eta)^q \quad (4)$$

where γ_o and γ_p are the Grüneisen parameter at atmospheric pressure and under high pressure, respectively, and *q* is the second Grüneisen parameter. *q* is assumed to be volume/pressure dependent (Nie 2000), in Eq. (5):

$$q = q_o(\eta)^n \quad (5)$$

q_o and q are second Grüneisen parameter at atmospheric pressure and under high pressure, respectively, with (n) is equal unity.

The effect of pressure on phonon frequency spectrum and density of states can be attributed as following.

Any reduction in the volume V_0 of a solid crystal causes a decrease in the equilibrium positions of the lattice bases; this consequently results in an increase in the frequency spectrum. Even if the compression is confined to the isotropic change in volume, vibrational frequencies will vary at least to two elastic constants, each of which will generally have a different dependence on the volume (Dlouha 1964). Thus, it is clear that a decrease in volume of the crystal is accompanied in a change of its frequency spectrum in a very complicated manner. However, if we consider all the difficulties in calculating the frequency spectrum of a crystal, it is unlikely to perform further calculations for different volumes. To show these obstacles to be overcome, at least approximately, Grüneisen approximation is a preferred consideration for interpreting the change in frequencies due to the compression of the solid crystal, which is represented in the following:

Equation 6 has been established (Al-Saqa and Al-Taie 2019;Sirwan et al. 2021; Dlouha 1964) for the relation between frequency ω and volume or pressure.

$$\omega_P = \omega(\eta)^{-\gamma} \tag{6}$$

where ω_p is the lattice frequency at pressure P. ω is the lattice frequency at atmospheric pressure.

And Eq. 7 for the variation of mode density under high pressure:

$$g_P(\omega_P, V_p) = \left(\frac{V_p}{V_o}\right)^{\gamma} g_o(\omega, V_o) \tag{7}$$

$g_p(\omega_P, V)$ and $g_0(\omega, V_o)$ are densities of state at high pressure P and at atmospheric pressure, respectively.

3 Calculation and Results

3.1 Evaluation of V_p/V_0 of C_{60}

B-M EOS (Eq. 1) and the nanoequation of state, namely S-K EOS, Eq. (2), have been used for describing V_p/V_0 for C_{60}. The input parameters, $K_0 = 18.1$ Gpa and $K'_0 = 5.7$ (Duclos et al. 1991), and the relative volume (V_p/V_0) values are substituted in the two EOSs (Eq. 1 and Eq. 2). High pressure has been evaluated and is shown in Fig. 1 in comparison with experimental data.

It can be seen from Fig. 1 that for lower pressure values up to 3 Gpa the two equations of state gave results for relative volume which fit relatively well with each other. Figure 1 shows the compatibility of the results of the well-known B-M EOS with the experimental data more closely than the results obtained with S-K EOS. This supports that the B-M EOS is valid for performing nanomaterial calculations just as good for performing bulk material calculations (Adnan et al. 2020).

3.2 Evaluation of Grüneisen Parameter (γ_p) Variation of C_{60} Under High Pressure

Calculating γ_p is achieved by combining Eqs. 4 and 5 with V_p/V_0 data given in Fig. 1 and using constant parameters values ($q_0 = 2.958$ and $\gamma_0 = 2.899$ (Singh and Gaur 2014). The variation of γ_p with high pressure p, according to B-M EOS, one time and, according to (nano) S-K EOS another time is obtained and illustrated in Fig. 2, where the results

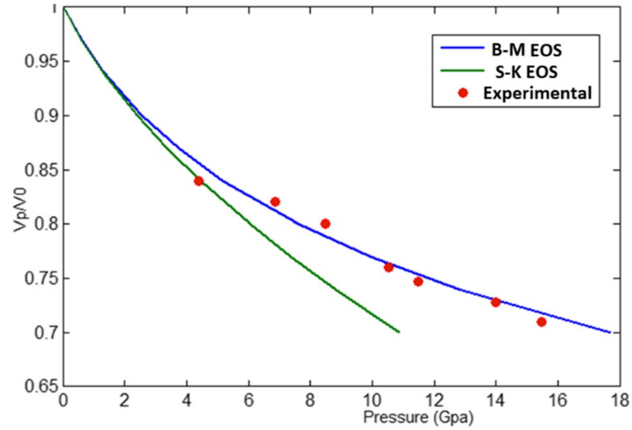


Fig. 1 C_{60} isotherm, evaluated by using different EOSs in comparison with experimental data (Duclos et al. 1991)

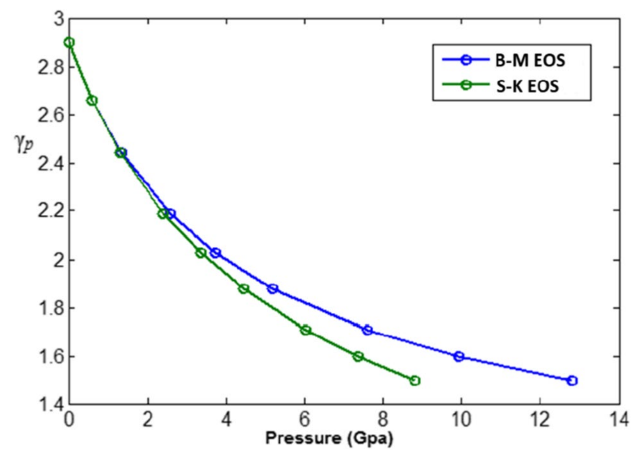


Fig. 2 Variation of Grüneisen parameter (γ_p) under high pressure of C_{60}, obtained with different EOSs

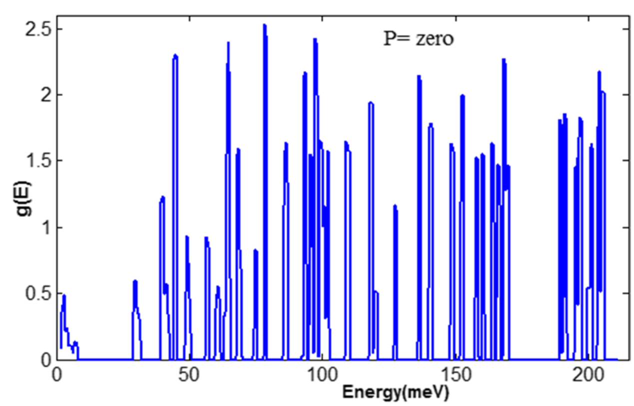
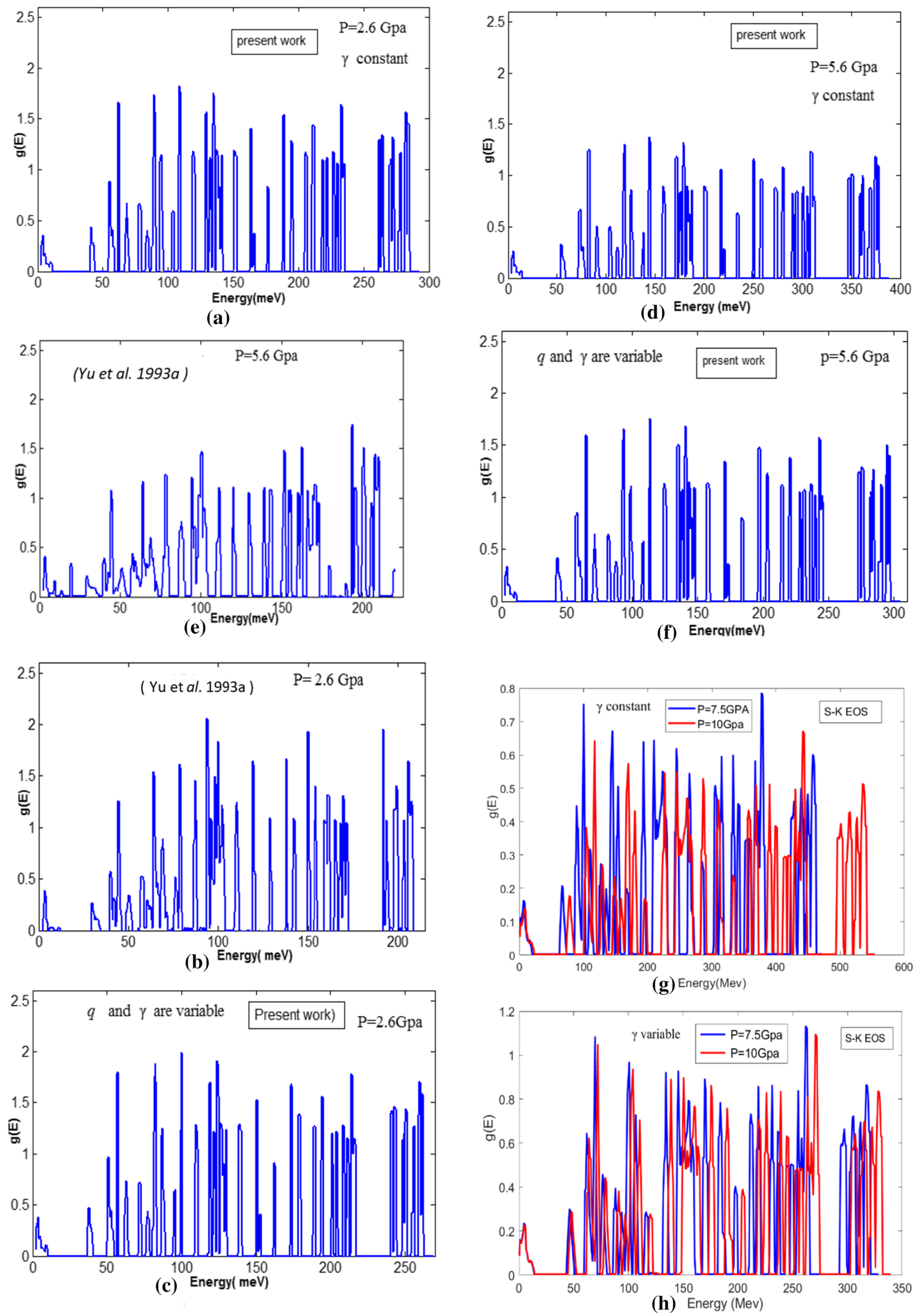


Fig. 3 Phonon frequency spectrum of C_{60} at atmospheric pressure (Yu et al. 1993b)


present work
P=2.6 Gpa
γ constant
g(E)
Energy(meV)
(a)
present work
P=5.6 Gpa
γ constant
g(E)
Energy (meV)
(d)
(Yu et al. 1993a)
P=5.6 Gpa
g(E)
Energy(meV)
(e)
q and γ are variable
present work
p=5.6 Gpa
g(E)
Energy(meV)
(f)
(Yu et al. 1993a)
P= 2.6 Gpa
g(E)
Energy(meV)
(b)
γ constant
P=7.5GPA
P=10Gpa
S-K EOS
g(E)
Energy(Mev)
(g)
q and γ are variable
Present work)
P=2.6Gpa
g(E)
Energy(meV)
(c)
γ variable
P=7.5Gpa
P=10Gpa
S-K EOS
g(E)
Energy (Mev)
(h)

◂**Fig. 4** Phonon frequency of solid C_{60} calculated according to the S-K EOS at: **a** $p=2.6$ Gpa —γ constant, **b** data of (Yu et al. 1993a) at $p=2.6$ Gpa, **c** improved present result at $p=2.6$ Gpa —γ and q are varied, **d** $p=5.6$ Gpa —γ constant, **e** data of (Yu et al., 1993a) at $p=5.6$ Gpa, **f** improved present result at $p=5.6$ Gpa —γ and q are varied, **g** $p=7.5$, 10 Gpa —γ constant, **h** improved calculated results at $p=7.5$, 10 Gpa Gpa, γ and q are variable

calculated by the two EOSs gave an accepted compatibility up to high pressure of 2 Gpa, while beyond this limit B-M EOS predicts higher required pressure for the same values of γ_p as required by the nano-EOS.

3.3 Evaluation of Phonon Frequency Spectrum of C_{60} Under High Pressure

Phonon frequency spectrum of C_{60} at ambient condition has been investigated throughout energy of around 220 meV (Yu et al. 1993b). The density of states is measured in arbitrary units, as shown in Fig. 3.

Pressure dependence of phonon frequencies and density of states are described in Grüneisen approximation with Eqs. 6 and 7. Two approaches are used for evaluating phonon frequency spectrum. Firstly assuming that the Grüneisen parameter ($\gamma_o=2.899$) is taken as a constant then:

1. Combining Eqs. 6 and 7 with V_p/V_0 data of S-K EOS in Fig. 1, and C60 phonon frequency spectrum data of Fig. 3 at ambient condition. Phonon frequency spectrum of C_{60} has been computed under high-pressure values, 2.6 Gpa, 5.6 Gpa,7.5 Gpa and 10 Gpa with S-K EOS as illustrated, in Fig. 4a, d respectively, in comparison with results of (Yu et al. 1993a) shown in Fig. 4b, e, respectively, while Fig. 4g shows comparison of obtained results for C_{60} pfs under (7.5 and 10) Gpa, as they were also evaluated on considering γ_o and q are constant.
2. Similarly, C_{60} phonon frequency spectrum has been computed with V_p/Vo data of B-M EOS shown in Fig. 1, and the obtained results are shown in Fig. 5a, d respectively, in comparison with results of (Yu et al. 1993a) shown in Fig. 5b, e respectively, while Fig. 5g shows comparison of obtained results for C_{60} pfs under (7.5 and 10) Gpa, as they were also evaluated on considering γ_o and q are constant.

Secondly: In order to improve the present obtained results of Figs. 4a, d, g and 5a, d, g and for the purpose of obtaining more agreement with data of (Yu et al. 1993a), variation of γ and q parameters under high pressure as given in Eqs. 4, 5 has been considered in evaluating C_{60} phonon frequency spectrum under high pressure. This is done by modifying Eqs. 6 and 7 to be in the forms of Eq. 8 and Eq. 9:

$$\omega_{P\gamma} = \omega(\eta)^{-\gamma_p} \tag{8}$$

$$g_{P\gamma}(\omega_{P\gamma}, V_p) = \left(\frac{V_p}{V_o}\right)^{\gamma_p} g_0\left(\omega, V_o\right) \tag{9}$$

where γ_p is given in Eq. 4 and shown in Fig. 2.

Improved results were obtained by using:

(1) S-K EOS:

Combining Eqs. 8 and 9 with V_p/V_o calculated values shown in Fig. 1 of S-K EOS and with Fig.3 data of C_{60} phonon frequency spectrum.

At p=2.6 Gpa, obtained improved phonon frequency spectrum is shown in Fig. 4c in comparison with (Yu et al. 1993a) data of Fig. 4b and a of present work—γ constant.

While at p=5.6 Gpa, Fig. 4f shows improved obtained result in comparison with Fig. 4e data (Yu et al. 1993a) and Fig. 4d of present work—γ constant.

For further clarification, Fig. 4h shows improved obtained results under high pressure (7.5 and 10) Gpa.

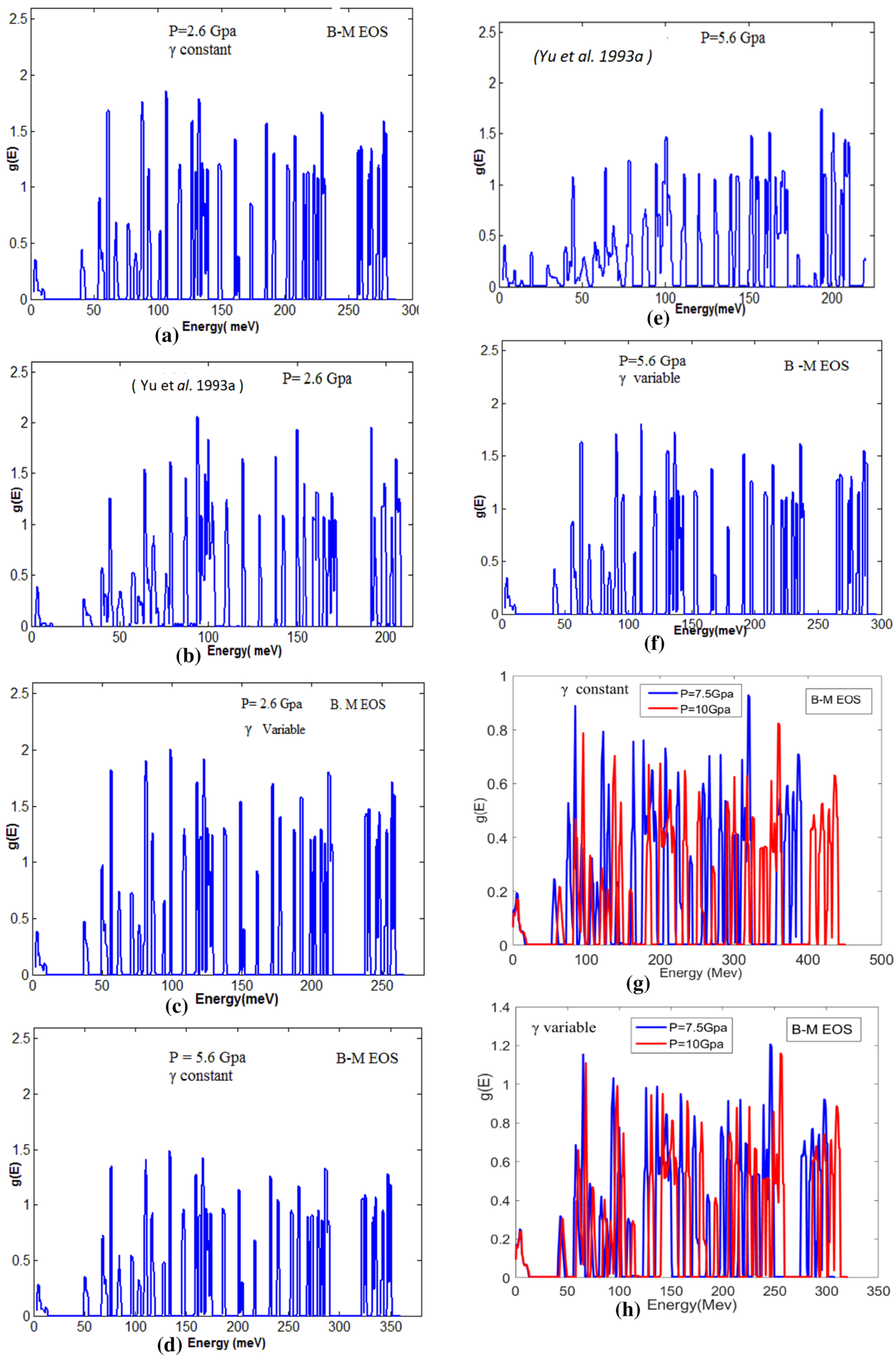
(2) B-M EOS:

On using B-M V_p/V_o data of Fig. 1 and Fig. 3 in Eqs. 8 and 9. At $p=2.6$ Gpa, obtained improved phonon frequency spectrum is shown in Fig. 5c in comparison with Fig. 5b data (Yu et al. 1993a) and Fig. 5a for result of present work—γ constant. For further clarification, Fig. 5h shows improved obtained results under high pressure (7.5 and 10) Gpa.

At $p=5.6$ Gpa, Fig. 5f shows obtained improved result in comparison with Fig. 5e data (Yu et al. 1993a) and Fig. 5d for result of present work, for which γ is considered constant.

4 Discussion and Conclusions

1. The results obtained in Fig. 1 using both S-K EOS and B-M EOS agree well at high pressures up to nearly 3 Gpa. But at higher pressure, the incompatibility between the results obtained using S-K EOS in calculating C60 isotherm and the experimental data of (Duclos et al. 1991) in Fig. 1 may be attributed to considering Bo' as a constant amount (Bo' = 4) from the beginning of the derivation of S-K EOS, while the results obtained using the well-known B-M EOS showed an excellent agreement with experimental data in Fig. 1. This was reflected in the results shown in Fig. 4, which obtained when calculating the variation of C_{60} phonon frequency spectrum under the influence of high pressure by combining S-K EOS with Grüneisen approximation, which showed less agreement with data of (Yu et al. 1993a) than it gave the



P=2.6 Gpa
γ constant
B-M EOS
g(E)
Energy(meV)
(a)
(Yu et al. 1993a)
P= 2.6 Gpa
g(E)
Energy(meV)
(b)
P= 2.6 Gpa
B. M EOS
γ Variable
g(E)
Energy(meV)
(c)
P = 5.6 Gpa
B-M EOS
γ constant
g(E)
Energy (meV)
(d)
P=5.6 Gpa
(Yu et al. 1993a)
g(E)
Energy(meV)
(e)
P=5.6 Gpa
B -M EOS
γ variable
g(E)
Energy(meV)
(f)
γ constant
P=7.5Gpa
P=10Gpa
B-M EOS
g(E)
Energy (Mev)
(g)
γ variable
P=7.5Gpa
P=10Gpa
B-M EOS
g(E)
Energy(Mev)
(h)

Fig. 5 Phonon frequency spectrum of C_{60} calculated with B-M EOS at: **a** $p=2.6$ Gpa —γ constant. **b** data of (Yu et al. 1993a) at $p=2.6$ Gpa, **c** improved present result at $p=2.6$ Gpa —γ and q are varied, **d** $p=5.6$ Gpa —γ constant, **e** data of (Yu et al. 1993a) at $p=5.6$ Gpa, **f** improved present result at $p=5.6$ Gpa —γ and q are varied, **g** $p=7.5$, 10 Gpa —γ constant, **h** improved calculated results at $p=7.5$, 10 Gpa, γ and q are variable

results shown in Fig. 5, which were obtained by combining B-M EOS with the Grüneisen approximation.

2. Grüneisen approximation approach is used for computing the effect of high pressure on the phonon frequency spectrum data. Under the application of high pressure, lattice frequencies/energies tend to shift to higher frequencies/energies, while mode density (density of states) peaks broaden and down to lower values as shown in Figs. 4 and 5 in comparison with Fig. 3. These results can be interpreted by the fact that when a solid is subjected to a high pressure strain may develop in the crystal which may modify the symmetry of the crystal and/or cause mixing between modes and these effects cause inactive modes to become active (Shearwood 1972).
3. The results obtained in Figs. 4 and 5 confirmed the importance of taking into account the pressure dependence of γ and q parameters. These results are also consistent with the theoretical conclusion mentioned by (Shearwood, 1972) that as applied high pressure on a solid increases more inactive modes become active.

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