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Thermoelastic Properties and Specific Heat Curve of C60 in Fcc Phase

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Abstracts

We have applied an Extended Three Body Force Shell Model (ETSM) for the investigation of thermoelastic properties such as cohesive energy(□□, molecular force constant(f), compressibility(□), Restrahlen frequency (□□), Debye temperature (□D), Gruneisen parameter (□), second Gruneisen parameter (q), Moelwyn Hughes constants (F1), and ratio of volume expansion coefficient (□v) to volume specific heat (cv) of C60 in Fcc phase. We have also reported the TOECs, pressure and temperature derivatives of SOECs. Here, we have measured the specific heat curve of C60. Here, we could compare our result with experimental data of neutron model and microcalorimeter data. Our computed specific heat results follow the same trends of variation with corresponding experimental data. The values of specific heats also increase with temperature. Our calculated results on specific heat are in closer agreement with the experimental data. Here, we could compare our result with other available data for some properties only at room temperature.

Keywords: Elastic Constants, Cohesive energy, Specific Heat.

Introduction

In the present decade, considerable interest has been taken in the investigation of anharmonic properties of materials of various kinds[1-2]. Many workers have contributed in the field through their experimental and theoretical approach. Several efforts have been made in the study of physical and anharmonic properties of solids of different types[3-6]. Utilizing different physical conditions and using several techniques. Some interesting results have been presented by several investigators while studying the anharmonic properties of the substances possessing various crystal structures. Some have studied temperature variation of anharmonic properties of mixed alkali halides and cyanides of rare gas materials[7]. of alkali halides[8-10]using ultrasonic[11-12]and Brillouin scattering[13] methods.

The static and dynamic structural properties of solid C_{60} are currently the subject of numerous investigations. At room temperature, the crystal has a face-centered cubic fcc structure, the fcc phase has the symmetry of the space group Fm3m with a lattice constant of a_0=14.2Å, where the C_{60} molecules rotate freely. With decreasing temperature, the rotational degrees of freedom of the C_{60} molecules becomes more and more hindered and the solid C_{60} undergoes a first order structural phase transition from orientationally disordered fcc phase to an orientationally ordered simple cubic structures with four molecules per unit cell located on four different cubic sub lattices having different orientations[14].

We have developed an Extended Three-Body Force Shell Model (ETSM), this model has successfully been applied to study the static, dynamic, dielectric, optical and anharmonic properties of pure ionic crystals, cyanides and alkali halide- cyanide mixed crystals having NaCl and CsCl structures. Looking to the considerable success of the ETSM[15-24], we have applied the ETSM to calculate the cohesive, thermal and elastic properties of C_{60}.
The essential formulation of the present model is given in the next section and input data, model parameters, results discussion and conclusions obtained by us are presented and discussed in the subsequent section.

Formulation

The interaction potential used to derive the framework of the present ETSM can be expressed as [25]

$$\phi = -\frac{e^2}{2}\sum_{kk'} Z_k Z_{k'} r_{kk'}^{-1}\left[1+\sum_{kk'} f_k\left(r_{kk'}\right)\right] - \sum_{kk'} c_{kk'} r_{kk'}^{-6} - \sum_{kk'} d_{kk'} r_{kk'}^{-8} - b\sum_{kk'} \beta_{kk'} \exp\left\{\frac{r_k + r_{k'} - r_{kk'}}{\rho}\right\} \quad (1)$$

where the first two terms represent the long range Coloumb and Three Body Interaction [26] the third and fourth terms are the van der Waals (vdW) interaction due to dipole-dipole (d-d) and dipole-quadrapole (d-q) attractions, the fifth term represents

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the Hafemeister Flygare[27] type short- range overlap repulsion extended up to second neighbour ions, $\beta_{kk'}$ are the Pauling coefficient[28] given by

$$\beta_{kk'} = 1 + \left(\frac{z_k}{n_k}\right) + \left(\frac{z_{k'}}{n_{k'}}\right) \quad (2)$$

with z_k (z_k') and n_k (n_k') as the valency and the number of effective electrons in the outermost orbit of the cations (anions).

The range and hardness (b and ρ) parameters determined from the equilibrium condition

$[d\phi(r)/dr]_{r=ro}=0$ (3)

Where r is the nearest interionic separation and r_o is the equilibrium separation and the bulk modulus,

$B=(9Kr_o)^{-1}[d^2\phi(r)/dr^2]_{r=ro}$ (4)

With K as the crystal structure constant (K=2 for NaCl structure).

a. Cohesive and Thermal properties: Cohesive energy (ϕ)of a material is a fundamental property, which tells us about the cohesion in the system. If the cohesion for the material is negative it means that the constituent atoms will gain energy by reacting to form a compound (solid or molecule). The binding energy in ionic crystals can be explained by calculating their cohesive energy from large number of interatomic interaction potentials. The details of these potentials have been reviewed earlier by [29-30]. The other parameters like molecular force constant (*f*), compressibility (β), Restrahlen frequency (υ_0), Debye temperature (θ_D), Gruneisen parameter (γ), Moelwyn Hughes constants (F_1) and ratio of volume thermal expansion coefficient (α_v) to volume specific heat (C_v) which are directly derived from the cohesive energy ϕ (r) are computed on the lines of Singh and Gaur [25].

$$\beta = \frac{3Kr_0}{f} \quad (5)$$

Where, K is the crystal structure constant (K=1.54 structure), r is the interatomic separation and f is the molecular force constant given as,

$$f = \frac{1}{3}\left[\phi''^{SR}_{kk'}(r) + \frac{2}{r}\phi'^{SR}_{kk'}(r)\right]_{r=r_0} \quad (6)$$

Where, ϕ" (r) and ϕ' (r) are second and first order derivatives of potential energy. The force constant, in turn, gives the Restrahlen frequency as,

$$\nu_0 = \frac{1}{2\pi}\left(\frac{f}{\mu}\right)^{1/2} \quad (7)$$

Where, μ is the reduced mass of the system.

In addition to cohesive properties, we have calculated the thermal properties for the C_{60} for the room temperature. In order to complete the test of any model, one has to apply it for the study of various thermal properties. Our model not only provides information about the temperature variation of thermal properties but also provide much insight into the intermolecular forces in solids. In this context, we have computed the Debye temperature (θ_D), Gruneisen parameter (γ), second Gruneisen parameter (q), ratio of volume expansion coefficient (α_v) to volume specific heat (c_v) and the Moelwyn Hughes constants (F_1).

The infrared absorption frequency (Reststrahlen frequency) ν_0 gives us the Debye temperature as,

$$\Theta_D = \frac{h\nu_0}{k} \quad (8)$$

Here h and k_B are Planck's and Boltzmann constant respectively. The Gruneisen parameter is given as,

$$\gamma = -\frac{r_0}{6}\left[\frac{\phi'''(r)}{\phi''(r)}\right]_{r=r_0} \quad (9)$$

Where, r is the interatomic separation, ϕ'''(r) and ϕ"(r) are the third and second order derivatives of potential energy. The second Gruneisen parameter is given as,

$$q = \gamma[1 + 2\gamma\alpha_v T] \quad (10)$$

The ratio of volume expansion coefficient α_v to the volume specific heat c_v is calculated from its well known expression,

$$\frac{\alpha_v}{c_v} = -\left[\frac{\phi'''(r)}{2r\phi''(r)}\right]_{r=r_0} \quad (11)$$

The Moelwyn Hughes constant (F_1) has been calculated from the relation,

$$F_1 = 1 - \frac{\beta}{27K}[\phi'''(r)]_{r=r_0} \quad (12)$$

b. Elastic properties: We have studied the anharmonic elastic properties by calculating Second Order Elastic Constants (SOECs), Third Order Elastic Constants (TOECs) as they provide physical insight into the nature of binding forces between the constituents of the crystal and are strongly related to other anharmonic properties, like thermal expansion, thermoelastic constants and thermal conductivity. The expression for these elastic constants and the pressure and temperature derivatives of SOECs are given by [31-35]

$$c_{111} = 32.237Tb\beta_T + \frac{e^2}{4r_0^4}[-32.231B_1 - 34.48B_2 + \frac{4C_1 - 12A_1 + C_2 - 3A_2}{4} + 13.4599B_1 + 89.305r_0 f'(r_0)] \quad (13)$$

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$$c_{112} = -4.15Tb\beta_T + \frac{e^2}{4r_0^4}[4.151B_1 + 4.52B_2 + \frac{C_2 - 3A_2}{8} + 4.6608r_0^2 f''(r_0) - 18.640r_0 f'(r_0)] \quad (14)$$

$$c_{166} = -6.151Tb\beta_T + \frac{e^2}{4r_0^4}[4.151B_1 + 4.52B_2 + \frac{C_2 - 3A_2}{8} - 3.5377B_{21} - 5.56r_0 f'(r_0)] \quad (15)$$

$$c_{123} = 2.332Tb\beta_T + \frac{e^2}{4r_0^4}[-2.332(B_1 + B_2) + 16.692r_0 f'(r_0)] \quad (16)$$

$$c_{144} = 2.332Tb\beta_T + \frac{e^2}{4r_0^4}[-2.332(B_1 + B_2) + 5.564r_0 f'(r_0)] \quad (17)$$

$$c_{444} = 2.332Tb\beta_T + \frac{e^2}{4r_0^4}[-2.332(B_1 + B_2)] \quad (18)$$

where $T\beta B_T = \frac{e^2}{4r^4}[1.165\varepsilon\{\varepsilon + 12f(r)\} + B_1 + B_2]$

and A_1, A_2, B_1, B_2 are the short range force parameters; f (r) and rf'(r) are the TBI parameters. The parameter f (r) and its derivatives are calculated from the knowledge of elastic constants and the $f = f_0 \exp(-r/\rho)$.

The expressions for the pressure derivatives of SOECs and TOECs are evaluated by using the expressions of second order, third order and fourth order elastic constants

$$\frac{dK}{dp} = -(3\Omega)^{-1}\left[\begin{matrix} 2.0350\varepsilon Z_m^2 + \frac{C_1 - 3A_1 + C_2 + 3A_2}{2} \\ -56.4032\varepsilon r_0 f'(r_0) + 24.433\varepsilon r_0^2 f''(r_0) \end{matrix}\right] \quad (19)$$

$$\frac{dS}{dp} = -(2\Omega)^{-1}\left[\begin{matrix} -5.2235\varepsilon Z_m^2 + A_1 - B_1 + \frac{C_2}{2} \\ +47.954\varepsilon r_0 f'(r_0) \end{matrix}\right] \quad (20)$$

$$\frac{dc_{44}}{dp} = -(\Omega)^{-1}\left[\begin{matrix} 1.2323\varepsilon Z_m^2 + \frac{A_1 - 7B_1 + C_1 + 3A_2 - 9B_2}{6} \\ -6.580\varepsilon r_0 f'(r_0) + 2.714\varepsilon r_0^2 f''(r_0) \end{matrix}\right] \quad (21)$$

$$\Omega = -0.3392\varepsilon Z_m^2 + \frac{A_1 + A_2}{2} + 9.4008\varepsilon r_0 f'(r_0)$$

$$S = \frac{c_{11} - c_{12}}{2}, \quad K = \frac{c_{11} - c_{12}}{3}$$

In addition to the pressure derivatives we have also evaluated the temperature derivatives of second order elastic constants [7] as given below

$$\frac{dc_{11}}{dT} = [c_{111} + 2c_{112} + 2c_{11} + 2c_{12}]\alpha_V \quad (22)$$

$$\frac{dc_{12}}{dT} = [c_{123} + 2c_{112} + c_{12}]\alpha_V \quad (23)$$

$$\frac{dc_{44}}{dT} = [c_{144} + 2c_{144} + 3c_{12} + 3c_{44}]\alpha_V \quad (24)$$

Where, α_v is the volume thermal expansion coefficient. Using these equations, we have computed the temperature derivatives of second order elastic constants for C_{60}

Input data and model parameters

Using the input data given in Table 1 for fcc C_{60} [36-37] we have calculated the model parameters listed in Table 2.

Table 1. Input data at 300K for C_{60}

S.No.	Properties	C_{60}
1	r (Å)	3.55 [a]
2	c_{11} (10^{11} dyn/cm^2)	2.64 [a]
3	c_{12} (10^{11} dyn/cm^2)	1.38 [a]
4	c_{44} (10^{11} dyn/cm^2)	1.17 [a]

a-[36]

Table 2. Model parameters at 300K for C_{60}

S.No.	Model Parameters	C_{60}
1	b (10^{12}erg)	4.164
2	ρ (Å)	0.2280
3	f (r)	-0.0041

Results and discussion

Results and discussion are given below in the next sections:

a. Lattice static properties: We have calculated the compressibility (β),molecular force constant (*f*), Reststrahlen frequency (ν_0) , Debye temperature (θ_D), Gruneisen parameter (γ), second Gruneisen parameter (q), Moelwyn Hughes constants (F_1), ratio of volume expansion coefficient (α_v) to volume specific heat (c_v), which are directly derived from the cohesive energy ϕ (r). The Table 2 shows that our values on cohesive energy and compressibility (β) are in good agreement with their available data [37]. The other thermodynamic properties listed in table 3 could not be compared due to lack of experimental data.

Table 3. Cohesive and Thermal properties of C_{60} at 300K

Properties	Values
ϕ(eV)	-1.096**(-1.99[b])**
β(10^{-12}dyn.cm^{-1})	1.669
f(10^4dyn.cm^{-1})	1.267
υ_0(THz)	3.807
Θ_D(K)	182.76

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$\alpha_V/c_V(10^3J)$	5.529
γ	2.899
Q	2.958
F_1	6.714

[b]-[37]

b. Anharmonic elastic properties: We have studied the anharmonic elastic properties by calculating Second Order Elastic Constants (SOECs), Third Order Elastic Constants (TOECs). We have calculated the TOECs for C_{60} probably for the first time at 300K are listed in Table 4. Our results on TOECs are found in good agreement with the available data[38]

Table 4. Values of pressure derivatives of SOECs and TOECs (10^{12} dyn/cm^2) of C_{60} at 300K

Properties	Values	Properties	Values
c_{111}	-7.997**(6.240)**[c]	dK/dP	16.14
c_{112}	-3.830**(-1.905)** [c]	dS/dP	2.977
c_{166}	-1.800**(-1.605)** [c]	dc_{44}/dP	-0.555
c_{123}	1.272 **(-1.80)** [c]	dc_{11}/dT	-5.176
c_{166}	1.021	dc_{12}/dT	-0.384
c_{456}	0.895	dc_{44}/dT	-0.092

[a] – [38]

c. Specific heat curve: We have reported the specific heat variation of C_{60} within the temperature range $0K \leq T \leq 400K$ and shown in Fig. 1 along with experimental results [39, 40]. Our computed specific heat as a function of temperature follow the similar trend as experimentally observed curve. The specific heat in the normal state of the material is usually approximated by the contribution of the lattice and electronic specific heat. In our ETSM model calculation, we have considered only the lattice contribution, which causes the discrepancy from measured specific heat curve. On the basis of above discussions, it may be concluded that ETSM has successfully explained the cohesive and thermal properties of C_{60}. The result on specific heat can further be improved by incorporating the electronic contribution in specific heat expression.

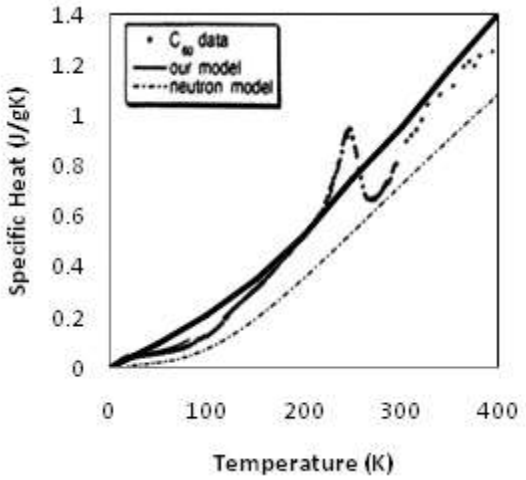

Figure 1: Variation of Specific heat of C_{60} in the temperature ranges $0K \leq T 400K$. The solid line (—) are calculated and compared with microcalorimeter (■) and neuton model(- -) results [39, 40].

Conclusion

The present ETSM has been applied, probably for the first time, to explore the elastic, cohesive and thermal properties of the orientationally disordered C_{60}. We have also applied our model for the calculation of specific heat curve. It can be concluded on the basis of the above result and discussions that the agreement between the experimental [37-40] and our theoretical results for elastic, cohesive and thermal properties are reasonably good for some of the parameters and some of them could not be compared due to lack of experimental data. A detailed description of the theoretical investigation of the second and higher order elastic, cohesive and thermodynamic properties of the orientationally disordered C_{60} has been presented in this paper. Here, some of the results on the higher order elastic constants and thermophysical parameters are of academic interest at present but they may serve as a guide to the experi- mental workers in future.

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