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Phonon dynamics of plutonium chalcogenides and pnictides

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ABSTRACT

We have investigated the phonon dynamics of the plutonium compounds (PuX; X = S, Se, Te, As, and Sb) by using rigid ion (RIM) and breathing shell models (BSM), later includes breathing motion of the electrons of the Pu-atoms due to *f*–*d* hybridization. We discuss the significance of these two approaches in predicting the phonon dispersion curves of PuX compounds and examine the role of electron–phonon interactions. Dominant ionic nature of bonding has been predicted for PuX compounds from the large LO–TO phonon splitting at zone center. We also report the one phonon density of states and first time calculated the lattice specific heat for these compounds.

1. Introduction

Considerable progress has been made in the past decade in the study of solid state properties of actinide compounds. The *5f* electrons of these compounds show variable behavior depending on the specific conditions being considered. In this regard, many studies have been carried out in actinides compounds to understand the role of their *5f* electrons during the application of pressure [1–7]. In the actinide series, Pu is considered to be the member where the *5f* electrons are involved in the metallic bonding at ambient condition and crystallize in the NaCl type structure. The main interest in PuX, however has been in their possible application in reactor technology. In the case of uranium pnictides, the lattice parameters, elastic and phonon properties are strongly related to the localized state of the *5f* electron of the uranium ion [8]. On the other hand plutonium is also related to the localized state of the *5f* electrons, and therefore, a comparison of the elastic and phonon properties of the uranium and plutonium compounds should give some information on the influence of the *5f* electron on the type of bonding in these compounds.

Earlier, the phonon dynamics and high pressure behavior of several uranium and rare-earth compounds [8,9] and the high pressure structural and elastic properties of plutonium compounds by using simple inter-atomic potential approach [10] have been reported by Srivastava and Sanyal [11]. Electronic structures of plutonium compounds have been investigated by Petit et al. [5] using SIC-LSD scheme within the Tight-Binding Linear-Muffin-Tin Orbitals (TB-LMTO) method [12]. In this investigation, the Pu *f*-electron manifold has been described in a mixed picture of localized and delocalized states.

In the present paper, we therefore attempt to explain the phonon properties of plutonium compounds PuX using the breathing shell (BSM) [13] and two-body rigid ion model (RIM) [13] which have been found to explain the phonon properties in uranium and other rare-earth compounds [8,9,14,15] successfully. These two models have different approaches as far as the interactions between ions are concerned. The present study will also be helpful in making qualitative understanding of electron–phonon interactions in this group of solids. We closely follow the method outlined in Ref. [13]. However, a brief description of the model theories and the methods of determination of the parameters are presented in Section 2. The results and discussion are presented in Section 3.

2. Theory

In the absence of any measured data on the phonon frequencies, optical and elastic properties, etc., we have selected two lattice dynamical models, namely the breathing shell model and rigid ion model [13] which have successfully explained the phonon properties of several uranium and rare-earth compounds [8–9,14–17]. In selecting the present models, we find the following arguments: (1) both models successfully predict the phonon properties of several uranium and rare-earth compounds; (2) since, one of our aim is to compare the structure of phonons in plutonium compounds with those in uranium compounds, similar models must be used; (3) the elastic constants reported by us previously [11] for Pu-compounds do not exhibit anomalous behavior, therefore, dominant ionic character is expected; (4) they have smaller number of parameters. The brief descriptions of the models are given below.

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Rigid ion model (RIM): The crystal potential energy in RIM is expressed as [13]

$$U(r) = 1/2\Sigma_{lk}\Sigma_{l'k'} Z_k Z_{k'} e^2/|r(lk;l'k')| + 1/2\Sigma_{lk}\Sigma_{l'k'} \Phi^R[|r(lk;l'k')|] \quad (1)$$

where the terms represent the usual two-body long-range Coulomb (first) and short range repulsive (second) potentials. In Eq. (1), $Z_k e$ and $Z_{k'} e$ denote ionic charges on kth and k'th ions, e is the electronic charge, $r(lk;l'k')$ is the distance between two ions at (lk) and $(l'k')$. This model has two short range parameters b and ρ are determined by minimizing potential energy $U(r)$ at equilibrium lattice constants (r_0) using expressions given by Srivastava and Sanyal [11].

The dynamical matrix corresponding to RIM is derived from Eq. (1) is expressed as [13]

$$\mathbf{D}(\mathbf{q}) = \mathbf{R} + \mathbf{Z\,C\,Z} \quad (2)$$

leading to secular determinant $|\mathbf{D}(\mathbf{q}) - \mathbf{Mw^2I}| = 0$. Here **R** and **C** are repulsive and Coulomb matrices, **Z** is a diagonal matrix ($3n \times 3n$) of charge, **M** is the mass matrix and $\boldsymbol{\omega}$ is the phonon frequency.

Breathing shell model (BSM): We have also chosen breathing shell model (BSM) which considers phenomenologically the short range electron–phonon interactions in terms of electron shell deformations. Depending upon symmetry, it includes dipolar, quadrapolar and breathing deformabilities of electron shell of the polarizable ions. A detailed review of these deformabilities is described in [13]. The dynamical matrix derived from interaction potential can be written as [13]

$$\mathbf{D}(\mathbf{q}) = (\mathbf{R}' + \mathbf{Z\,C\,Z}) - (\mathbf{R}' + \mathbf{ZCY})(\mathbf{R}' + \mathbf{K} + \mathbf{YCY})^{-1}(\mathbf{R}'^{+} + \mathbf{YCZ}) \quad (3)$$

where $\mathbf{R}' = (\mathbf{R} - \mathbf{QH}^{-1}\,\mathbf{Q}^{+})$, **C** and **R** are the Coulomb and short range repulsive interaction matrices. **Q** is a (6×2) matrix representing the breathing mode variable while **H** is a (2×2) matrix specifying the interactions between the breathing mode variables of different ions in the lattice. **K** and **Y** are the diagonal matrices and represent the core–shell interaction and shell charge, respectively. The present version of BSM has eight parameters, and can be self-consistently determined from crystal properties. The experimental values of dielectric constants and zone center phonon frequencies (ν_{TO}) for plutonium compounds (PuX) are not available, so we have calculated these frequencies (ν_{TO}) by scaling method. We have scaled transverse optical phonon frequency (ν_{TO}) of these compounds by the known values of zone center phonon frequencies of homologous series of uranium compounds (UX; X = S, Se, Te, As and Sb) using following equation:

$$\frac{(\omega_{TO})^2_{PuX}}{(\omega_{TO})^2_{UX}} = \frac{\mu_{UX}}{\mu_{PuX}} \quad (4)$$

where $(\omega_{TO})_{PuX}$ and $(\omega_{TO})_{UX}$ are the transverse optical phonon frequencies, while μ_{PuX} and μ_{UX} are the reduced masses of plutonium and uranium compounds, respectively. The elastic constants have been calculated by us by using the measured values of bulk modulus and lattice parameters [11]. The input data and model parameters for both models (RIM and BSM) are listed in Tables 1–3.

Table 1
Input constants for plutonium compounds. Elastic constants are in 10^{11} N/m^2, frequency in THz, lattice parameter (a) in nm, polarizabilities α_1 and α_2 in 10^{-30} m^3.

Properties	PuS	PuSe	PuTe	PuAs	PuSb
a	0.55436[a]	0.57930[b]	0.61838[b]	0.58580[b]	0.62410[b]
C_{11}*	2.1635	2.2086	0.7989	1.4565	1.4299
C_{12}*	0.5604	0.4014	0.1586	0.3202	0.2453
C_{44}*	0.5880	0.4133	0.1654	0.3337	0.2549
ν_{T0} (Γ)	9.48	6.19	4.72	5.97	4.68
α_1[c]	0.32	0.43	0.36	0.38	0.34
α_2[c]	2.90	3.77	5.50	4.31	6.60
ε_o[d]	5.448	8.087	6.434	7.200	7.605
ε_∞*	2.385	2.7059	3.129	2.922	3.747

[a] Ref. [18].
[b] Ref. [5].
[c] Ref. [19].
[d] Ref. [20].
* Calculated values.

Table 2
Model parameters for plutonium compounds (RIM). All force constants are in units of $e^2/2$ V and lattice parameter (a) in nm.

Properties	PuS	PuSe	PuTe	PuAs	PuSb
a	0.5543	0.5793	0.6183	0.5858	0.6241
A_{12}	40.82	43.20	20.88	32.04	30.56
B_{12}	−4.228	−3.741	−1.890	−3.070	−3.001
A_{11}	−0.422	−0.432	−0.310	−0.363	−0.308
B_{11}	0.073	0.069	0.047	0.050	0.046
A_{22}	2.452	1.846	1.150	1.971	1.744
B_{22}	−0.179	−0.112	−0.072	−0.112	−0.079
Z_m	1.92	1.82	1.30	1.66	1.64

Table 3
Model parameters for plutonium compounds for breathing shell model (all force constants are in units of $e^2/2$ V, Z and Y in units of e).

Properties	PuS	PuSe	PuTe	PuAs	PuSb
A_{12}	46.52	55.06	33.198	41.18	43.137
B_{12}	−3.537	−6.5554	−5.3278	−5.019	−3.3204
A_{11}	2.9138	8.8178	9.9016	7.1576	3.580
B_{11}	−2.039	−2.6391	−1.5298	−3.1395	−2.5415
B_{22}	0.1297	−0.4339	1.407	0.32924	0.07304
Z_m	1.92	1.82	1.30	1.66	1.64
$Y_1 = Y_2$	−69.3972	9.3677	14.378	16.637	−65.83
$G_1 \times 10^2$	6404.33	97.32	339.20	366.07	7743.85
$G_2 \times 10^2$	709.03	10.76	21.76	31.85	3999.39

3. Results and discussion

In the present investigation, we have calculated phonon frequencies for three plutonium chalcogenidies (PuS, PuSe and PuTe) and two plutonium pnictides (PuAs and PuSb) using rigid ion model (RIM) and breathing shell model (BSM) discussed above. The ionic polarizibilites of anion and cation for both the models have been derived from the known value of ε_0 of uranium compounds and using LST relation [16]. The calculated phonon dispersion curves (PDC) for these compounds from RIM and BSM are plotted in Fig. 1a–e. It is seen from these figures that the present models explain some of the phonon modes satisfactorily. These figures show that both LO and TO phonons at Γ point calculated from both the models are non-degenerate, unlike the uranium compounds, though the ν_{TO} and dielectric properties for the Pu-compounds have been derived from U-compounds after proper scaling. From our calculation, we obtain a large gap in the LA and TA frequencies at the X and L-points for the PuX (X = S, Se, Te, As, and Sb) compounds as compared to uranium compounds. A possible reason for such large gap in the LA and TA can be polarizibilities of cation as well as small magnitude of C_{12} and C_{44}. The large splitting between LO and TO frequency for PuX at L-point reveals it failure to take proper account of short range interaction. However, the calculated values of all phonon modes from RIM, in general, stay above the BSM results except PuTe. This fact can be attributed to the non-inclusion of electronic polarizibilites in RIM. In case of

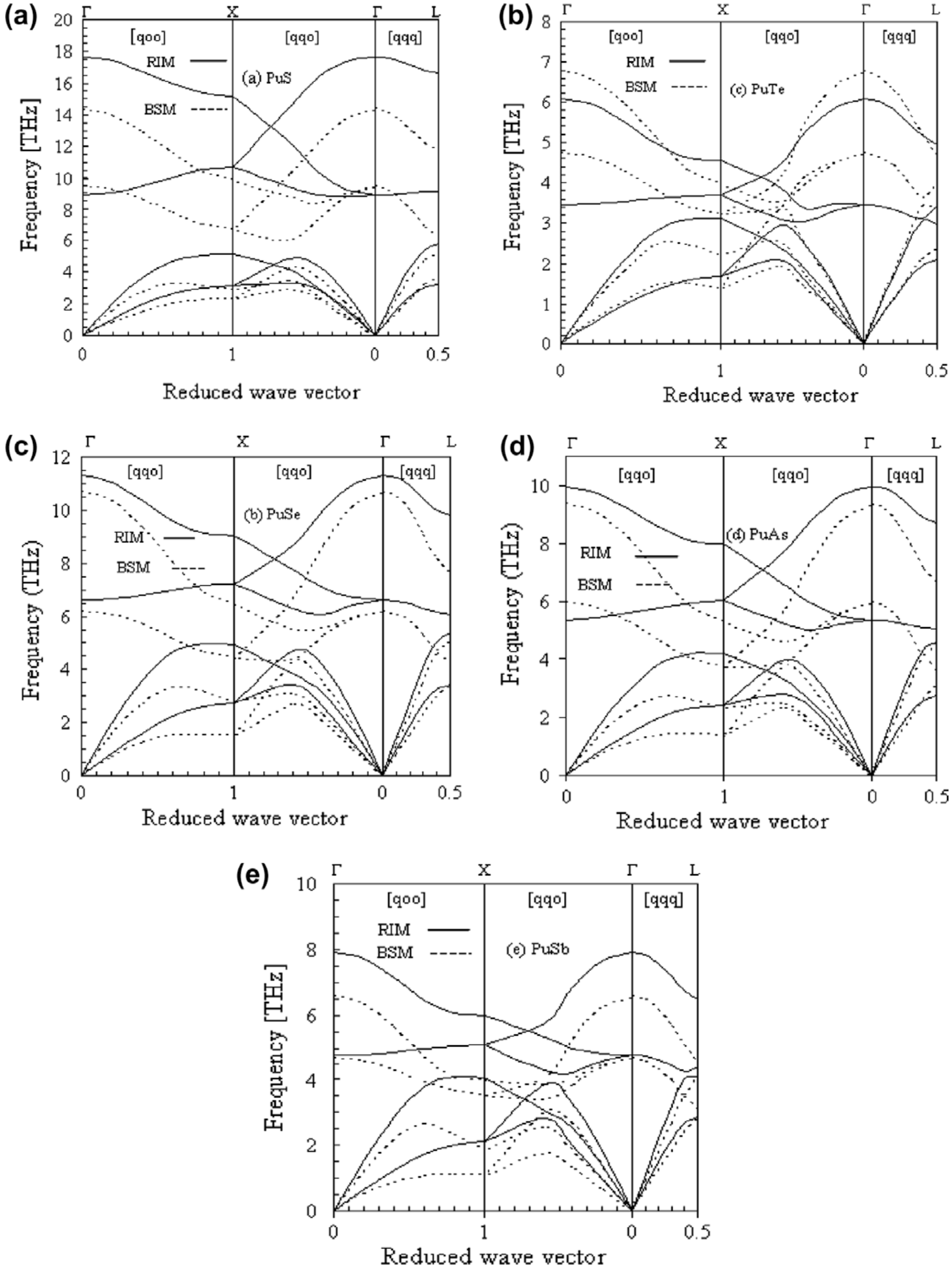

Fig. 1. Phonon dispersion curves using RIM and BSM for (a) PuS, (b) PuSe, (c) PuTe, (d) PuAs, and (e) PuSb. Solid (—) and dashed (- - -) curves represent PDC for RIM and BSM, respectively.

PuS, the acoustic modes obtained from BSM are in general smaller than those predicted from RIM. Moreover, BSM predicts maximum LA frequencies around [.6 0 0]. This fact clearly shows electronic polarizibilites must be incorporated in future calculation of phonons in such compounds. Similar arguments, as pointed out earlier [17], are in general, applicable to all other plutonium compounds studied in the present paper. In the case of PuTe, splitting between LA and TO mode at *L*-point is quite similar to that of PuS, but gradually decreases from PuS to PuTe which is probably due to large ionic size and atomic mass of cations. Similar conclusion can also be drawn in the case of dispersion curves for PuAs and PuSb Fig. 1d and e. For the sake of comparison we have tabulated the calculated frequencies of PuX and UX compounds obtained from RIM (TRIM for UX) and BSM at zone center (Γ) and zone boundaries (X and L) in Tables 4a and 4b, 5a and 5b for a realistic comparison. At Γ point, the LO frequencies obtained from present RIM and BSM

Table 4a
Γ and X point frequencies (THz) of plutonium chalcogenides.

Solids		Γ-point		X-point			
		LO	TO	LO	TO	LA	TA
PuS Pre.	BSM	14.33	9.48	9.90	6.66	2.85	2.30
	RIM	17.68	8.87	15.17	10.7	5.13	3.17
US Theo.	BSM[a]	9.54	9.54	9.25	8.90	2.29	1.30
	TRIM[a]	9.25	9.25	10.4	10.02	2.95	1.38
	Expt.[b]	9.54	9.54	9.25	8.90	1.70	2.05
PuSe Pre.	BSM	10.7	6.19	6.49	4.40	2.78	1.48
	RIM	11.31	6.63	9.03	7.23	4.92	2.72
USe Theo.	BSM[a]	6.20	6.20	5.85	5.75	2.24	1.30
	TRIM[a]	6.00	6.00	6.80	6.05	2.03	0.96
	Expt.[b]	6.20	6.20	6.00	5.90	1.90	1.75
PuTe Pre.	BSM	6.77	4.72	3.96	3.23	2.22	1.38
	RIM	6.07	3.44	4.54	3.69	3.11	1.69
UTe Theo.	BSM[a]	4.74	4.74	3.93	4.21	1.89	1.02
	TRIM[a]	4.60	4.60	5.23	4.75	1.65	0.85
	Expt.[b]	4.74	4.74	4.30	4.30	1.25	1.50

[a] Ref. [21].
[b] Ref. [23], Pre. → present, Theo. → theoretical.

Table 4b
L-point frequencies (THz) of plutonium chalcogenides.

Solids		LO	TO	LA	TA
PuS Pre.	BSM	11.83	6.32	5.13	3.62
	RIM	16.66	9.07	5.78	3.22
US Theo.	BSM[a]	9.27	8.36	3.28	3.29
	TRIM[a]	9.29	9.35	3.30	2.78
	Expt.[b]	8.95	8.90	3.15	3.15
PuSe Pre.	BSM	7.69	5.05	4.25	3.34
	RIM	9.81	6.09	5.38	3.42
USe Theo.	BSM[a]	5.62	5.00	3.10	3.09
	TRIM[a]	6.44	5.14	2.20	2.60
	Expt.[b]	5.80	5.85	3.10	3.09
PuTe Pre.	BSM	4.67	3.95	3.36	2.35
	RIM	4.94	3.41	2.97	2.11
UTe Theo.	BSM[a]	4.05	4.00	2.80	2.81
	TRIM[a]	4.82	3.89	1.79	2.37
	Expt.[b]	4.05	4.05	2.10	2.37

[a] Ref. [21].
[b] Ref. [23], Pre. → present, Theo. → theoretical.

Table 5a
Γ and X point frequencies (THz) of plutonium pnictides.

Solids		Γ-Point		X-Point			
		LO	TO	LO	TO	LA	TA
PuAs Pre.	BSM	9.36	5.96	5.35	3.72	2.34	1.34
	RIM	9.96	5.39	7.98	6.04	4.19	2.43
UAs Theo.	BSM[a]	5.99	5.99	5.54	5.47	2.77	1.65
	TRIM[a]	5.99	5.99	6.21	6.20	3.30	1.85
	Expt.[b]	5.99	5.99	5.56	5.50	2.65	1.90
PuSb Pre.	BSM	6.58	4.68	3.99	3.49	1.86	1.09
	RIM	7.92	4.78	6.00	5.08	4.04	2.13
USb Theo.	BSM[a]	4.76	4.76	4.85	4.55	2.42	1.70
	TRIM[a]	4.66	4.66	5.21	4.87	2.21	1.66
	Expt.[b]	4.76	4.76	4.70	4.70	2.10	1.80

[a] Ref. [21].
[b] Ref. [23], Pre. → present, Theo. → theoretical.

calculation for PuX compounds are quite similar. However, these frequencies differ considerably along X- and L-point of the Brillouin zone. The calculated frequencies obtained from RIM and BSM are different in magnitudes as the former includes only ionic polarizabilities while the later includes both ionic and electronic polarizabilities in its equation of motion. Hence, the latter model (BSM) is more realistic and valid. A comparison of the magnitude of the frequencies of PuX and UX, calculated from both model shows that in the former class of solids, they are larger but consistent with the models considered for them.

In Fig. 2a–e, we have plotted the one phonon density of states of all five PuX compounds obtained from both BSM and RIM models.

Table 5b
L-point frequencies (THz) of plutonium pnictides.

Solids		LO	TO	LA	TA
PuAs Pre.	BSM	6.66	4.55	3.61	3.05
	RIM	8.72	5.06	4.63	2.75
UAs Theo.	BSM[a]	5.34	5.24	3.00	2.88
	TRIM[a]	5.56	5.56	3.35	2.88
	Expt.[b]	5.34	5.25	3.27	2.85
PuSb Pre.	BSM	4.55	4.05	3.09	2.77
	RIM	6.49	4.41	4.11	2.86
USb Theo.	BSM[a]	4.83	4.54	2.79	2.78
	TRIM[a]	5.11	4.35	2.21	2.68
	Expt.[b]	4.83	4.76	2.79	2.79

[a] Ref. [21].
[b] Ref. [23], Pre. → present, Theo. → theoretical.

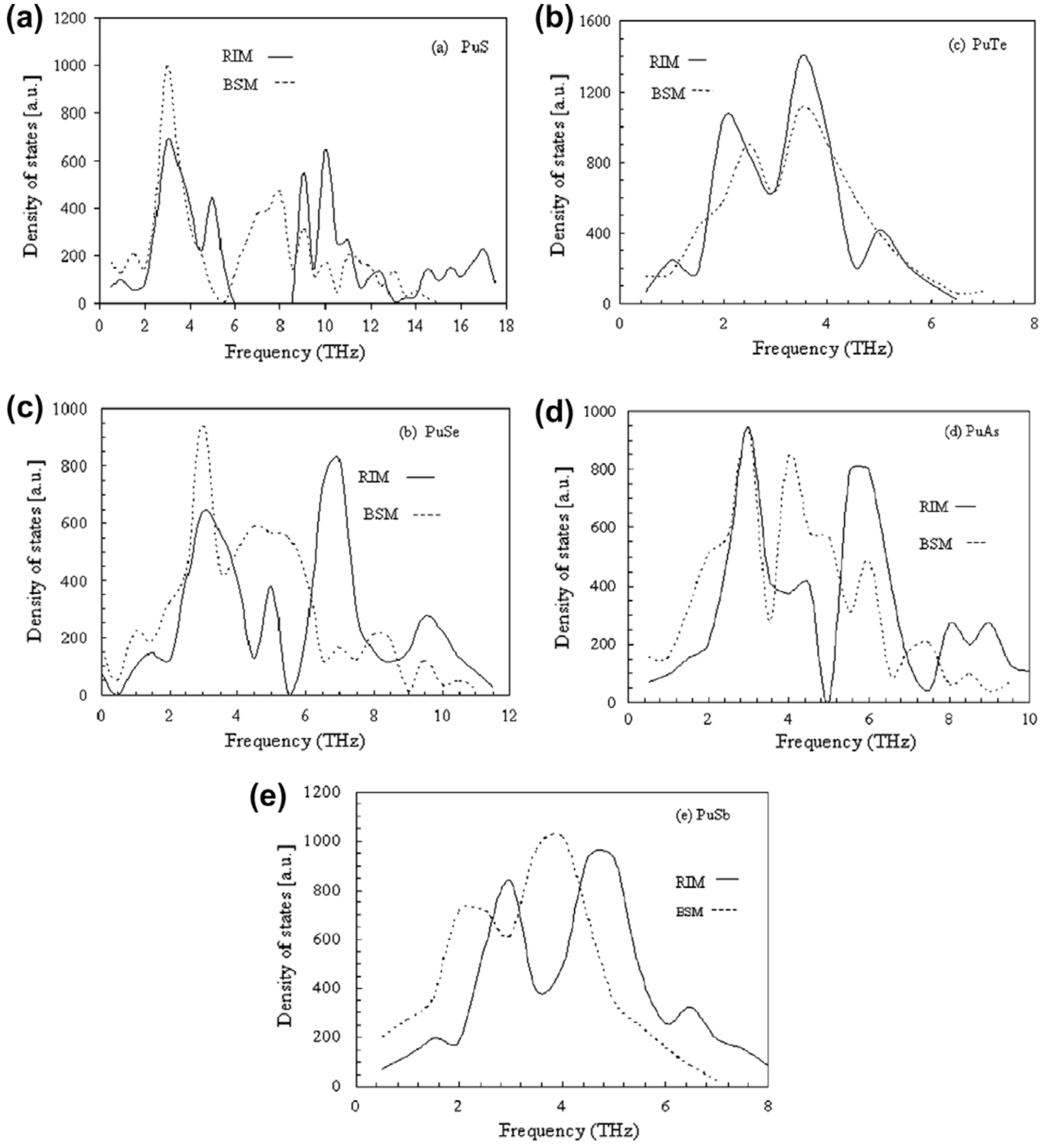

Fig. 2. One phonon density of states using RIM and BSM for (a) PuS, (b) PuSe, (c) PuTe, (d) PuAs, and (e) PuSb. Solid (—) and dashed (- - -) curves are for RIM and BSM, respectively.

A comparison between the peak positions obtained from both the models reveals that they show similar peaks but shifted in frequency. Also the magnitudes of density of states are consistent and comparable. In case of PuS, the density of states is nearly zero between 6.0 and 8.5 THz. Both models depict the gross features of the density of states in this group (PuSe, PuTe, PuAs, and PuSb). In the absence of any experimental data, relative merit of either of the model calculation cannot be judged at this moment. We believe

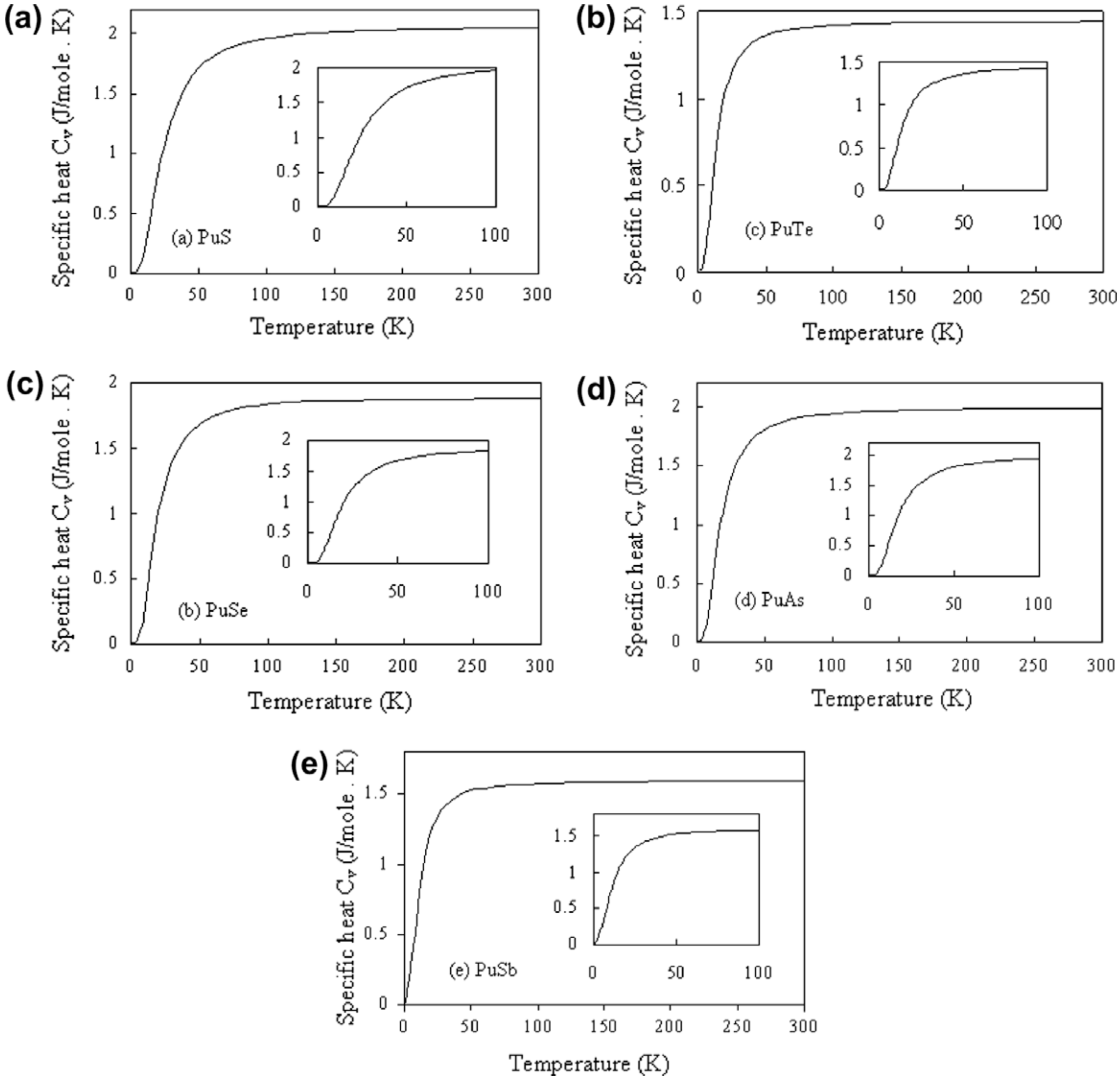

Fig. 3. Specific heat at constants volume (C_v) as a function of temperature using BSM for (a) PuS, (b) PuSe, (c) PuTe, (d) PuAs, and (e) PuSb.

that these results will be quite useful to the experimentalists. In Fig. 3a–e, we have presented the calculated low temperature specific heat of all PuX compounds at constant volume as a function of temperature. The specific heat has been calculated using standard Debye theory [22]. We do not observe any anomalous behavior in this property. In general, the predicted phonon dispersion curves of PuX show similar gross features, which are nearly similar to those of uranium compounds [1].

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