Indian Journal of Pure & Applied Physics
Vol. 53, February 2015, pp. 98-101

Lattice dynamical properties of neptunium chalcogenides

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Received 30 June 2013; revised 18 April 2014; accepted 20 October 2014

The phonon calculations of neptunium chalcogenides (NpX; X = S, Se, Te) based on breathing shell model (BSM) which includes breathing motion of electron of the Np-atoms due to *f-d* hybridization, have been performed. The significance of this approach in predicting the phonon properties of NpX compounds has been discussed and the role of *f*-electron has been examined. The model predicts that the short range breathing phenomenon plays a dominant role in the phonon properties. The specific heat for these compounds has been reported.

Keywords: Phonon dispersion, Specific heat of solids, Phonon-electron interaction

1 Introduction

The neptunium chalcogenides (NpX; X = S, Se, Te) crystallize in NaCl structure and exhibit a wide variety of physical phenomena that are of great interest to solid state scientists. These neptunium compounds posses striking similarities and differences in their physical properties as compared to the other rare-earth series. But due to the difficulties encountered in handling these radioactive materials, relatively little is known about their structural and mechanical properties as compared to the technologically important elements like uranium and plutonium[1-3]. They display numerous allotropic structures and properties and lend themselves to several systematic studies of physical properties as a function of the distance between metal atoms and lattice constants. One physical property common to both uranium and neptunium compounds is that, both atoms have unfilled *f* electron shells and the energy of this band is nearly degenerate in two configuration i.e. $4f^{n}$ $(5d6s)^{m}$ and $4f^{n-1}$ $(5d6s)^{m+1.}$ This causes a strong electron-phonon interaction in these systems of solids. The lattice parameters, elastic and phonon properties of uranium chalcogenides are strongly related to the localized state of the *5f* electron of the uranium ion[4]. The neptunium is also related to the localized state of the *5f* electron, therefore, a comparison of the elastic and phonon properties of the uranium and neptunium compounds should give some information on the influence of the *5f* electron and the type of bonding in these compounds.

The high pressure structural properties of the mono-chalcogenides of neptunium have been investigated by using experimental techniques such as high pressure X-ray diffraction[5-8], optical reflectivity measurements[9-11] etc, but fewer investigations by using the theoretical approaches have been performed[12]. Most of these studies exhibit that the degree of *5f* localization is a factor which determines the structure, lattice constants and elastic properties of these compounds. Some of our earlier work on the phonon dynamics, high pressure behaviour of several uranium and rare-earth compounds[13,14], the high pressure structural and elastic properties of neptunium compounds by using simple inter-atomic potential[15], have been reported by Jha *et al*[16]. In the present paper, the phonon properties of neptunium chalcogenides (NpX ; X = S, Se, Te) have been explained using the breathing shell model[17] (BSM) which has been found to explain the phonon properties in uranium and other rare-earth compounds[13,18-20] successfully. The present study will also be helpful in making qualitative understanding of phonons in this group of solids and draw some conclusions regarding the role of *f*-electrons.

2 Theory of Model Applied

In the absence of any measured data on the phonon frequencies, optical and elastic properties etc., the lattice dynamical model has been selected, namely the breathing shell model[17] which has successfully explained the phonon properties of several uranium and rare earth compounds[13,14,18-20]. In selecting this model, we find the following arguments: (1) This model successfully predicts the phonon properties of several uranium and rare earth compounds; (2) To compare the structure of phonons in neptunium compounds with those in uranium compounds, similar model must be used; (3) The elastic constants reported by us previously[16] for Np-compounds do not exhibit anomalous behaviour, therefore, dominant ionic character is expected; (4) They have smaller number of parameters. The 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, quadra polar and breathing deformabilities of electron shell of the polarizable ions. A detailed review of these deformabilities is described in physics report[17]. The dynamical matrix derived from interaction potential can be written as[17]:

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

where $R' = (R - QH^{-1}Q^{+})$, 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.

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

Properties	NpS	NpSe	NpTe
r_o	0.5532[a]	0.5804[b]	0.6198[c]
C_{11}^{*}	1.254	0.8109	1.197
C_{12}^{*}	0.5930	0.4990	0.3855
C_{44}^{*}	0.6207	0.4990	0.3855
$\upsilon_{T0}(\Gamma)$	9.48	6.19	4.72
α_1^{d}	0.318	0.442	0.366
α_2^{d}	2.900	3.770	5.500
$\varepsilon_o^{e} = \varepsilon_\infty$	5.448	8.087	6.434

[a]Ref.5, [b]Ref. 8, [c]Ref. 7, [d]Ref. 21, [e]Ref. 22, * Calculated value

Table 2 — Model parameters for neptunium compounds calculated using Breathing Shell Model (all force constants are in units of $e^2/2V$, Z and Y in units of e)

Properties	NpS	NpSe	NpTe
A_{12}	49.47	50.31	46.94
B_{12}	-7.830	-9.346	-8.705
A_{11}	3.326	1.956	3.234
B_{11}	-2.426	-2.730	-3.335
B_{22}	0.318	0.443	0.366
Z_m	1.70	1.73	1.30
$Y_1=Y_2$	-4.004	-4.497	-4.293
$G_1\times10^2$	21.39	22.32	29.9
$G_2\times10^2$	0.697	0.805	0.766

3 Results and Discussion

The phonon frequencies for NpS, NpSe and NpTe have been calculated using the breathing shell model (BSM). The input data and model parameters for this model are listed in Tables 1 and 2, respectively. The experimental values of frequencies (v_{TO}) are not available. Therefore, these frequencies (v_{TO}) by scaling method, have been calculated. The transverse optical phonon frequency (v_{TO}) of these compounds has been scaled by the known values of zone centre phonon frequencies of homologous series of uranium compounds (UX; X= S, Se and Te) using the following equation:

$$\frac{(\omega_{TO})^2_{NpX}}{(\omega_{TO})^2_{UX}} = \frac{\mu_{UX}}{\mu_{NpX}} \qquad \ldots(2)$$

where $(\omega_{TO})_{NpX}$ and $(\omega_{TO})_{UX}$ are the transverse optical phonon frequencies, while μ_{NpX} and μ_{UX} are the reduced masses of neptunium and uranium compounds, respectively. The elastic constants have been calculated by us by using the measured values of bulk modulus and lattice parameters[16]. The calculated phonon dispersion curves (PDC) for three NpX have been presented in Figs 1(a-c). The present model explains the phonon mode satisfactorily (Fig. 1). In the case of NpS, the acoustic modes along three symmetry directions are satisfactorily reproduced by BSM model is revealed from Fig. 1(a). The optical frequencies in all the symmetry directions for NpS have been satisfactorily explained by BSM, except minor discrepancy at L point. The splitting of phonons at X and L point depicts the role of ionic polarizabilites at the zone boundaries. BSM predicts maximum LA frequencies around (6,0,0). This fact clearly shows electronic polarizablities which must be incorporated in future calculation of phonons in such compounds. Similar arguments, as pointed out earlier, are in general, applicable to other two NpSe and NpTe compounds studied in the present paper. Our theoretical prediction of optical branches for NpTe from the present model theory (BSM) is not entirely satisfactory, as was in the case of NpS and NpSe. In the case of NpTe, BSM more or less satisfactorily explains both LO and TO phonon along [q00] and [qqq] directions. But along [qq0] large discrepancy is observed. This model also predicts the LA and TA branches along [qqq] to be non-generate. For the sake of comparison, we have tabulated the calculated frequencies of NpX and UX compounds obtained from BSM at zone center (Γ) and zone boundaries (X and L) in Table 3 (a and b). At Γ point, the LO frequencies obtained from present BSM calculation for NpX compounds are quite similar. However, these frequencies differ considerably along X-and L-point of the brillouin zone. A comparison of the magnitude of the frequencies of NpX and UX, calculated from this model shows that in the former class of solids, they are larger but consistent with the models considered for them. The phonon density of states is an important vibration property as its computation needs phonon frequencies in the entire brillouin zone. The one phonon density of states of all three NpX compounds obtained from both BSM model has been plotted in Fig. 2(a-c). In case of NpS, the density of states is nearly zero between 4.5 to 6.5 THz. This model depicts the gross features of the density of states in this group (NpSe, NpTe). In the absence of any experimental data, relative merit of either of the model calculation cannot be judged at this moment. We believe that these results will be quite useful to the experimentalists. The calculated values of specific heat at constant volume as function of temperature are shown in Fig. 3(a-c). At lower and higher temperature, the model predicts similar trend of variation of specific heats of all NpX compounds. In the inset, we plot the variation of specific heat at low temperature. The specific heat has been calculated

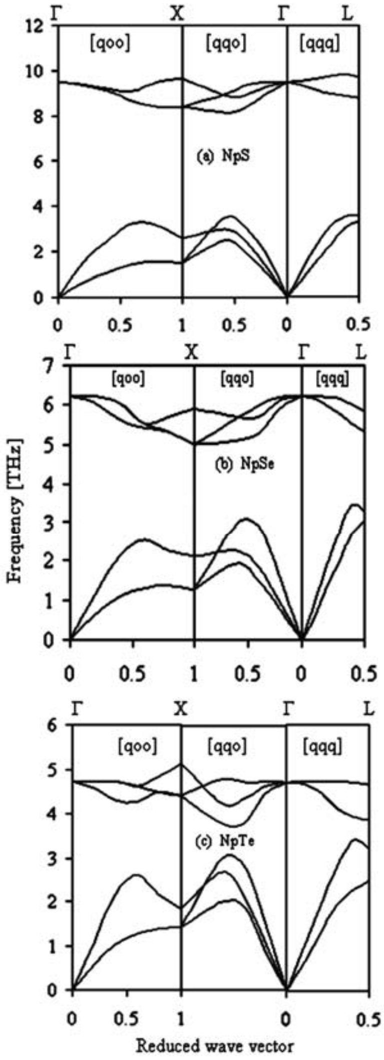

Fig. 1 — Phonon dispersion curves using BSM for (a) NpS, (b) NpSe, (c) NpTe

Table 3(a) — Γ and X point frequencies (THz) for NpS, NpSe and NpTe

Solids	Γ-Point		X-Point			
	LO	TO	LO	TO	LA	TA
NpS Present	9.50	9.50	9.71	8.30	2.70	1.70
US Theory[f]	9.54	9.54	9.25	8.90	2.29	1.30
Experiment[g]	9.54	9.54	9.25	8.90	1.70	2.05
NpSe Present	6.23	6.23	6.05	5.10	2.38	1.33
USe Theory[f]	6.20	6.20	5.85	5.75	2.24	1.30
Experiment[g]	6.20	6.20	6.00	5.90	1.90	1.75
NpTe Present	4.71	4.71	5.09	4.50	1.92	1.47
UTe Theory[f]	4.74	4.74	3.93	4.21	1.89	1.02
Experiment[g]	4.74	4.74	4.30	4.30	1.25	1.50

[f]Ref.[23], [g]Ref.[4]

Table 3(b) — L point frequencies (THz) for NpS, NpSe & Np Te

	L-Point			
Solids	LO	TO	LA	TA
NpS Present	9.88	8.90	3.86	3.62
US Theory[f]	9.27	8.36	3.28	3.29
Experiment[g]	8.95	8.90	3.15	3.15
NpSe Present	6.10	5.50	3.42	3.19
USe Theory[f]	5.62	5.00	3.10	3.09
Experiment[g]	5.80	5.85	3.10	3.09
NpTe Present	4.72	4.00	3.30	2.68
UTe Theory[f]	4.05	4.00	2.80	2.81
Experiment[g]	4.05	4.05	2.10	2.37

[f]Ref.[23], [g]Ref.[4]

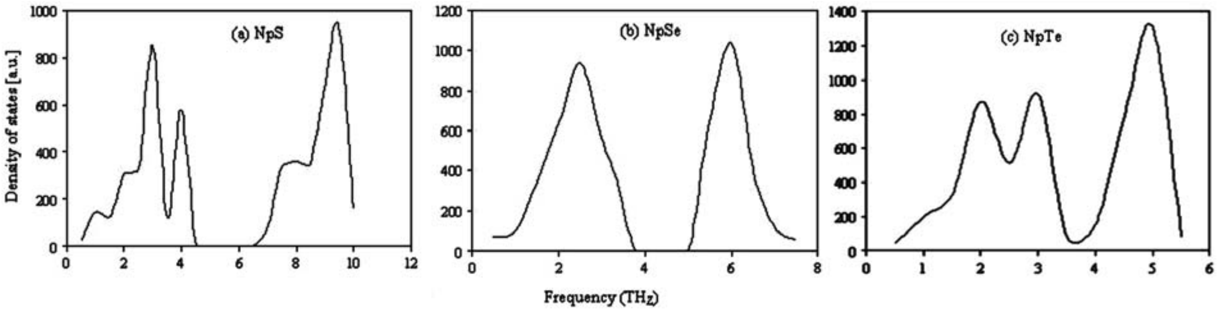

Fig. 2 — One phonon density of states using BSM for (a) NpS, (b) NpSe and (c) NpTe

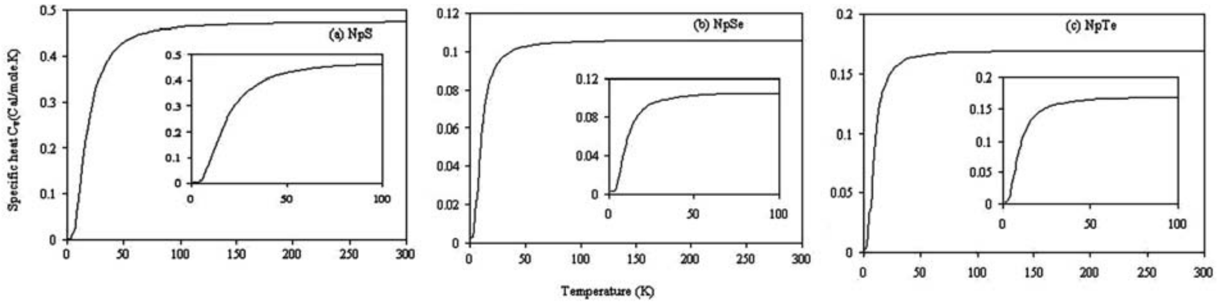

Fig. 3 — Specific heat at constants volume (C_V) using BSM for (a) NpS, (b) NpSe and (c) NpTe

using standard Debye theory[24]. Any anomalous behaviour in this property has not been observed. In general, the predicted phonon dispersion curves of NpX show similar gross features, which are nearly similar to those of uranium compounds.

Acknowledgement

The work has been financially support by University Grants Commission(UGC), New Delhi and MPCST. The authors are thankful to Department of Higher Education, Bhopal for providing facilities.

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