Lithuanian Journal of Physics, Vol. **46**, No. 3, pp. 355–359 (2006)

EFFECT OF VAN DER WAALS INTERACTIONS ON THE PHONON DYNAMICS IN USe

Atul Pandey [a] and K.S. Upadhyaya [b]

[a] *Department of Physics, K. N. Govt. P. G. College Gyanpur, Sant Ravidas Nagar Bhadohi-221304, Uttar Pradesh, India*
[b] *Smt. Indira Gandhi Government Degree College, Lalganj, Mirzapur, Uttar Pradesh, India*
E-mail: kripa1shankar@yahoo.com

Received 28 April 2006

Van der Waals three body force shell model (vTSM), which includes the effect of van der Waals interactions (vWI) and three body interactions in the framework of both ions polarizable rigid shell model (RSM), has been employed to study the crystal dynamics of USe. We assume that the overlap repulsion is effective only up to the first neighbour, while the van der Waals attraction acts up to the second neighbours and plays very important role. The agreement between our predictions and experimental data for phonon dispersion curves strongly supports the inclusion of van der Waals interactions. We also report the specific heat variations, two phonon IR / Raman spectra, and anharmonic properties of USe.

Keywords: Lattice vibrational properties, phonons, dispersion curves

PACS: 63.20.-e, 65.40.Ba, 78.30.-j

1. Introduction

The NaCl-type uranium monochalcogenides (US, USe, and UTe) show a great variety of interesting physical phenomena and some of them exhibit strong anomalies in the phonon spectra. The nature of these compounds can be well understood by high energy gap, high dielectric constants, and large negative-ion electronic polarizabilities (α^-). Jackman et al. [1] have reported the experimental results on phonon dispersion relations and Rudigier et al. [2–3] have reported on specific heat variations for USe. Jackman et al. [1] have fitted the rigid ion and shell models (RIM and SM) to neutron scattering data but the agreement obtained by them is poor particularly at X point. The RIM and SM also fail to explain Cauchy violation ($C_{12} \neq C_{44}$) for USe. Lattice dynamics of uranium chalcogenides (including USe) have been studied by Jha et al. [4] by using three body force rigid ion model which includes long range three body interactions due to charge transfer effects [5] but three body force rigid ion model (TRIM) has failed to explain phonon anomalies in these compounds. In another attempt, Jha and Sanyal [6] employed three body force rigid shell model which incorporated long range three body interactions in the framework of rigid shell model. The three body force shell model (TSM) has explained the phonon discrepancies slightly better than the three body force rigid ion model (TRIM) but still discrepancies are observed along $(q00)$ and $(qq0)$ directions. Further, TSM could not explain the zero splitting of optical phonon frequency at X point. Later on, Jha and Sanyal [7] have employed breathing shell model [8] in which they considered the breathing motion of electron shells. They also compare their results with TRIM and neutron scattering data; although the results are better than those reported by using TRIM and TSM, yet they are not entirely satisfactory and failure of the model can be seen more along $(q00)$ for optical branches. Further, breathing shell model (BSM) less satisfactorily explains the discrepancies observed along $(qq0)$ direction. In order to explain the lattice vibrational behaviour of USe better, the present authors have employed a model vTSM which includes the effects of van der Waals interactions and three body interactions in the framework of both ions polarizable rigid shell model. This model has already been used for the study of lattice dynamics of lead chalcogenides [9] and US [10] .

2. Theory

The general formalism of van der Waals three body force shell model, vTSM, can be derived from the

ISSN 1648-8504

crystal potential whose relevant expression per unit cell is given by

$$\Phi = \Phi^{\mathrm{C}} + \Phi^{\mathrm{R}} + \Phi^{\mathrm{TBI}} + \Phi^{\mathrm{vWI}} , \qquad (1)$$

where the first term Φ^{C} is Coulomb interaction potential and is long-range in nature, the second term Φ^{R} is short-range overlap repulsion potential, the third term Φ^{TBI} is three body interactions potential, and the last term Φ^{vWI} is van der Waals interaction potential and owes its origin to the correlations of the electron motions in different atoms.

Using the crystal expression (1) and introducing the effect of van der Waals interaction (vWI) and three body interactions (TBI), the secular determinant

$$|\mathbf{D}(q) - \omega^2 \mathbf{M}\mathbf{I}| = 0 \qquad (2)$$

is obtained for the frequency determination, where $\mathbf{D}(q)$ is the 6×6 dynamical matrix, $\mathbf{M}$ is the diagonal matrix representing the ionic masses, and $\mathbf{I}$ represents unit 6×6 matrix.

If we consider the second neighbour dipole–dipole van der Waals interaction energy, then it is expressed as

$$\Phi^{\mathrm{vWI}}_{\mathrm{dd}}(r) = -S_{\mathrm{v}} \left| \frac{C_{++} + C_{--}}{6r^6} \right| = \Phi^{\mathrm{v}}(r) , \qquad (3)$$

where S_{v} is a lattice sum and the constants C_{++} and C_{--} are the van der Waals coefficients corresponding to the positive–positive and negative–negative ion pairs, respectively. A detailed theory of present model (vTSM) has been reported elsewhere [10].

3. Computations and results

We have calculated our twelve model parameters by using interatomic separation r_0, elastic constants C_{11}, C_{12}, and C_{44}, frequencies $\nu_{\mathrm{LO}}(\Gamma) = \nu_{\mathrm{TO}}(\Gamma)$, $\nu_{\mathrm{LO}}(\mathrm{L})$, $\nu_{\mathrm{TO}}(\mathrm{L})$, $\nu_{\mathrm{LA}}(\mathrm{L})$, and $\nu_{\mathrm{TA}}(\mathrm{L})$, electronic polarizabilities α_1 and α_2, and van der Waals coefficients C_{++}, C_{--} and have presented them in Table 1. These parameters have been employed to calculate the phonon dispersion curves for USe and have been shown in Fig. 1. The calculated phonon dispersion curves (PDC) have also been compared with the experimental data [1]. The adequacies of van der Waals three body force shell model (vTSM) have been further tested by studying specific heat variations and two phonon IR / Raman spectra. For this we have computed the specific heats at constant volume and pressure (C_{v}/T and C_{p}/T) from the phonon spectra, plotted against the square of temperature (T^2), and presented along with measured data in Fig. 2. In order to study the second order IR and Raman spectra we have employed the critical point analysis [11]. A comparison of combined density of states (CDS) peaks and their assignments from IR / Raman scattering spectra with the help of neutron data [1] and the present study is shown in Table 2. We have also studied the anharmonic elastic properties by calculating third and fourth order elastic constants as they provide physical insight into the nature of binding forces between the constituents of a crystal. The expressions

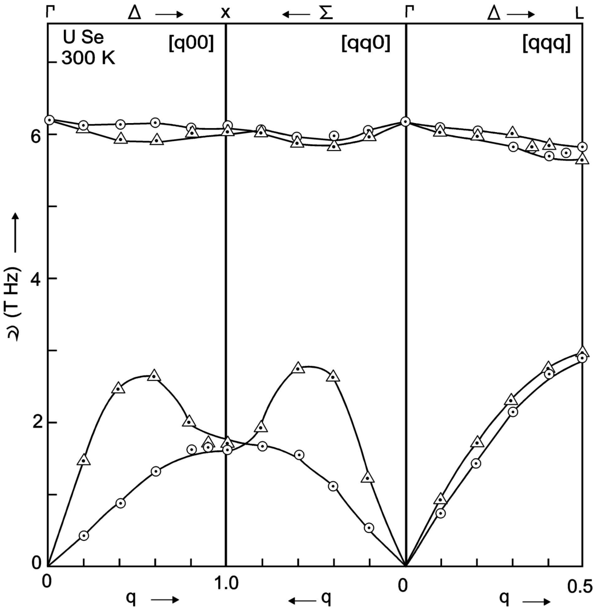

Fig. 1. Phonon dispersion curves for USe: △ are longitudinal, ⊙ are transverse experimental points, — is present study.

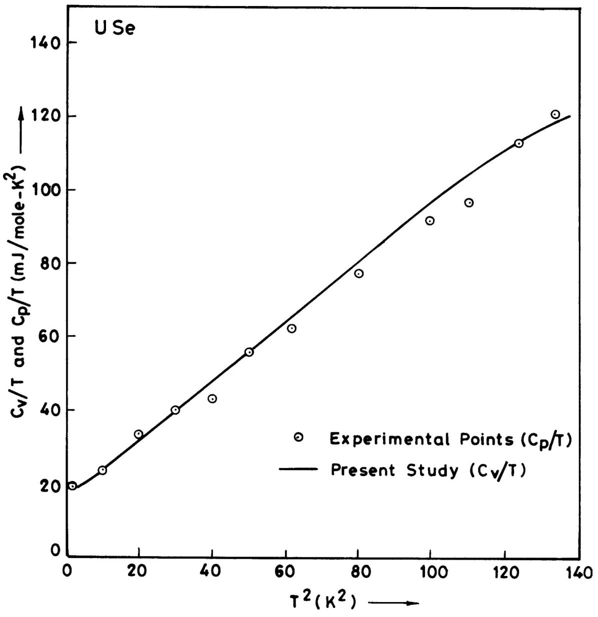

Fig. 2. Specific heat at constant volume and pressure (C_{v}/T and C_{p}/T) as a function of T^2.

Table 1. Input data and model parameters for USe.

Properties	Values	Ref.	Parameters	Values
C_{11} (10^{12} dyne/cm^2)	2.01	[7]	Z_{m}^2	2.0821
C_{12} (10^{12} dyne/cm^2)	0.00	[7]	$r_0 f_0'$	−0.1076
C_{44} (10^{12} dyne/cm^2)	0.17	[7]	A_{12}	37.6977
$\nu_{\mathrm{LO}}(\Gamma) = \nu_{\mathrm{TO}}(\Gamma)$ (THz)	6.20	[1]	B_{12}	−2.8709
$\nu_{\mathrm{LO}}(\mathrm{L})$ (THz)	5.88	[1]	A_{11}	−11.3557
$\nu_{\mathrm{TO}}(\mathrm{L})$ (THz)	5.90	[1]	B_{11}	21.2040
$\nu_{\mathrm{LA}}(\mathrm{L})$ (THz)	2.97	[1]	A_{22}	8.2385
$\nu_{\mathrm{TA}}(\mathrm{L})$ (THz)	2.96	[1]	B_{22}	−20.7587
r_0 (10^{-8} cm)	2.87	[7]	d_1	0.2196
α_1 (10^{-24} cm^3)	0.41	[7]	d_2	1.6625
α_2 (10^{-24} cm^3)	7.00	[7]	Y_1	−3.4909
C_{++} (10^{-60} erg cm^6)	1428	[13]	Y_2	−7.8724
C_{--} (10^{-60} erg cm^6)	792	[13]		

Table 2. Assignments of two-phonon Raman and infra-red peaks for USe.

CDS peaks (cm^{-1})	Raman active			Infra-red active		
	Peaks, Ref. [1] (cm^{-1})	Present study		Peaks, Ref. [1] (cm^{-1})	Present study	
		Assignments	Values (cm^{-1})		Assignments	Values (cm^{-1})
57	–	–	–	–	–	–
107	110	2TA(Δ)	104	110	2TA(Δ)	104
		2TA(X)	110	–	–	–
125	123	LA+TA(Δ)	120	123	LA+TA(Δ)	120
143	146	TO–TA(Δ)	148	–	–	–
	147	TO–LA(X)	140	–	–	–
		LO–LA(X)	143	–	–	–
165	–	–	–	–	–	–
193	194	2TA(L)	194	–	–	–
	196	LA+TA(L)	199	–	–	–
230	–	–	–	–	–	–
247	–	–	–	–	–	–
260	258	LO+TA(Δ)	257	258	LO+TA(Δ)	257
	259	TO+TA(X)	255	–	–	–
		LO+TA(X)	258	–	–	–
	261	TO+LA(X)	261	–	–	–
		LO+LA(X)	263	–	–	–
288	–	–	–	288	TO+TA(L)	289
				290	TO+LA(L)	294
298	–	–	–	295	LO+LA(L)	300
327	–	–	–	–	–	–
355	–	–	–	–	–	–
388	387	LO+TO(L)	390	–	–	–
	392	2LO(L)	396	–	–	–
407	406	2LO(Δ)	410	406	2LO(Δ)	410
	408	2TO(X)	400	–	–	–
		LO+TO(X)	403	–	–	–
		2LO(X)	406	–	–	–

Table 3. Third and fourth order elastic constants (in units 10^{12} dyne/cm^2) for USe.

Property	Value	Property	Value
C_{111}	684.9202	C_{1122}	2.1527
C_{112}	−0.3420	C_{1266}	2.5310
C_{166}	−0.5598	C_{4444}	2.3288
C_{123}	0.3273	C_{1123}	−0.8834
C_{144}	0.4288	C_{1144}	−1.2409
C_{456}	0.4795	C_{1244}	−1.0417
C_{1111}	783.6910	C_{1456}	−1.2181
C_{1112}	0.4296	C_{4456}	−0.9702
C_{1166}	1.8076		

Table 4. Values of pressure derivatives of SOE and TOE constants for USe.

Property	Value
$\mathrm{d}K/\mathrm{d}P$	6.5750
$\mathrm{d}S/\mathrm{d}P$	8.2181
$\mathrm{d}C_{44}/\mathrm{d}P$	−1.0571
$\mathrm{d}C_{111}/\mathrm{d}P$	−1409.5924
$\mathrm{d}C_{112}/\mathrm{d}P$	−1.3347
$\mathrm{d}C_{166}/\mathrm{d}P$	1.9728
$\mathrm{d}C_{123}/\mathrm{d}P$	1.8301
$\mathrm{d}C_{144}/\mathrm{d}P$	0.0140
$\mathrm{d}C_{456}/\mathrm{d}P$	2.1024

for these elastic constants and pressure derivatives of second order elastic constants (SOEC) are similar to those derived by Puri, Verma, and Garg [12] for NaCl structure. The third order (C_{111}, C_{112}, C_{166}, C_{123}, C_{144}, C_{456}) and fourth order (C_{1111}, C_{1112}, C_{1166}, C_{1122}, C_{4444}, C_{1123}, C_{1144}, C_{1244}, C_{1456}, C_{4456}) elastic constants are shown in Table 3, while the pressure derivatives of second and third order elastic constants ($\mathrm{d}C_{44}/\mathrm{d}P$, $\mathrm{d}C_{111}/\mathrm{d}P$, $\mathrm{d}C_{112}/\mathrm{d}P$, $\mathrm{d}C_{166}/\mathrm{d}P$, $\mathrm{d}C_{123}/\mathrm{d}P$, $\mathrm{d}C_{144}/\mathrm{d}P$, and $\mathrm{d}C_{456}/\mathrm{d}P$) of USe have been presented in Table 4.

4. Discussion and conclusion

The computed phonon dispersion curves displayed in Fig. 1 show that the inclusion of van der Waals interaction have improved the agreement between experimental data [1] and our results. The inclusion of van der Waals interaction (vWI) with TBI have influenced both longitudinal and transverse optic modes much more than acoustic branches. The agreement between theory and experimental data at X point is also excellent. Another striking feature of the present model is noteworthy from the excellent reproduction of almost all branches. Hence the predictions of phonon dispersion curves (PDC) for USe using vTSM may be considered more satisfactory than those from other models [1, 4, 6–7].

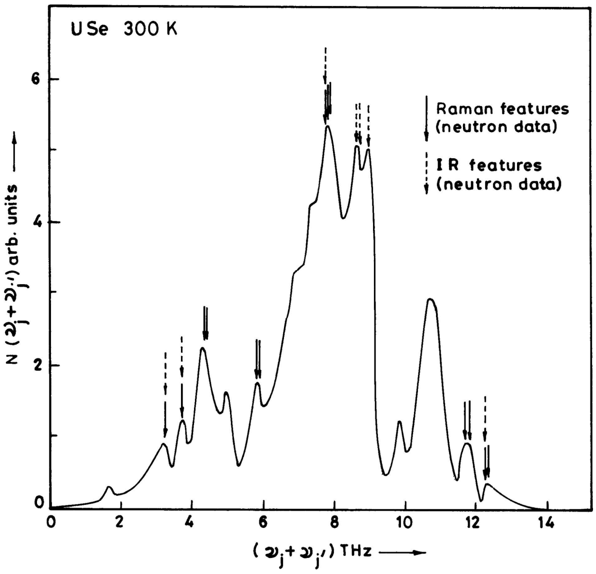

Fig. 3. Combined density of states curve for USe.

We have plotted the variation of specific heat at constant volume and pressure (C_v/T and C_p/T) with the square of temperature (T^2). It is evident from the Fig. 2 that our results are in good agreement with measured data [2] and are generally better than those of breathing shell model (BSM) [6]. The combined density of states by using vTSM for USe has been plotted in Fig. 3. The basic aim of the study of two phonon IR / Raman scattering spectra is to correlate the neutron and optical experimental data for USe. We have also investigated the anharmonic properties of USe by using vTSM. This includes the predictions of third and fourth order elastic constants and the pressure derivatives of SOE and TOE constants. Since no experimental values on these properties have been reported so far, we are unable to comment as such on the reliability of our results.

In this paper we have systematically reported phonon dispersion curves, specific heat variations, combined density of states, and anharmonic properties of USe. On the basis of overall fair agreement, it may be concluded that the present model, van der Waals three body force shell model (vTSM), is adequately capable to describe the crystal dynamics of USe.

Acknowledgements

The authors are grateful to the computer centre, B.H.U., Varanasi for computational assistance. They are also indebted to Prof. S.P. Sanyal and Dr P.K. Jha for many useful discussions.

References

[1] J.A. Jackman, T.M. Holden, and W.J.L. Buyers, Systematic study of the lattice dynamics of the uranium rocksalt-structure compounds, Phys. Rev. B **33**, 7144–7153 (1986).

[2] H. Rudigier, H.R. Ott, and O. Vogt, Low-temperature specific heat of uranium monopnictides and monochalcogenides, Phys. Rev. B **32**, 4584–4591 (1985).

[3] H. Rudigier, H.R. Ott, and O. Vogt, Low-temperature specific heat of uranium monopnictides and monochalcogenides, Physica B **130**, 538–540 (1985).

[4] P.K. Jha and S.P. Sanyal, Lattice dynamics of uranium chalcogenides and pnictides, Phys. Rev. B **46**, 3664–3667 (1992).

[5] R.K. Singh, Many-body interactions in binary ionic solids, Phys. Rep. **85**, 259–401 (1982).

[6] P.K. Jha, R.K. Singh, and S.P. Sanyal, Phonon anomalies in uranium chalcogenides, Physica B **174**, 101–104 (1991).

[7] P.K. Jha and S.P. Sanyal, Lattice vibrational properties of uranium chalcogenides, Physica B **216**, 125–131 (1995).

[8] V. Nusslein and U. Schroder, Calculations of dispersion curves and specific heats for LiF and NaCl using the breathing shell model, Phys. Status Solidi B **21**, 309–314 (1967).

[9] K.S. Upadhyaya, M. Yadav, and G.K. Upadhyaya, Lattice dynamics of IV–VI ionic semiconductors: An application to lead chalcogenides, Phys. Status Solidi B **229**, 1129–1138 (2002).

[10] K.S. Upadhyaya, Atul Pandey, and D.M. Srivastava, A study of the phonon properties of uranium monochalcogenides: US as an example, Chinese J. Phys. **44**(20), 127–136 (2006).

[11] C. Smart, G.R. Wilkinson, A.M. Karo, and J.R. Hardy, *Lattice Dynamics*, ed. R.F. Wallis (Pergamon Press, Oxford, 1965).

[12] D.S. Puri, V.K. Garg, and M.P. Verma, Many-body effects on 3rd-order elastic constants and pressure derivatives of 2nd-order elastic constants of CsCl structure solids, Phys. Status Solidi B **78**, 113–122 (1976).

[13] L.P. Sharma, PhD thesis, Agra University, Agra, India (1979).

VAN DER VALSO SĄVEIKŲ ĮTAKA USe FONONŲ DINAMIKAI

Atul Pandey [a], K.S. Upadhyaya [b]

[a] *Valstybinis koledžas, Džanpūras, Indija*
[b] *Indiros Gandi valstybinio laipsnio koledžas, Lalgandžas, Indija*

Santrauka

Van der Valso (van der Waals) trijų kūnų sąveikos sluoksninis modelis, apimantis van der Valso sąveikų įtaką ir trijų kūnų sąveikas pagal abiejų jonų poliarizuojamų kietų sluoksnių modelį, panaudotas tirti USe kristalų gardelės dinamikai. Tariama, kad stūma dėl sanklotos veikia tik pirmuosius kaimynus, o tuo tarpu van der Valso trauka veikia ir antruosius ir yra labai svarbi. Teoriškai numatytų rezultatų ir eksperimentiškai gautų duomenų apie fononų dispersijos kreives sutapimas patvirtina, kad turi būti atsižvelgiama į van der Valso sąveikas. Taip pat pateiktos savitosios šilumos variacijos, dvifononiai IR ir Ramano spektrai ir anharmoninės USe savybės.