A Study of the Phonon Properties of Uranium Monochalcogenides: US as an Example

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A twelve parameter model vTSM (van der Waals three body force shell model), which includes the effect of van der Waals interactions (vWI) and three body interactions in the framework of a polarizable rigid shell model (RSM) for both ions, has been employed for a comprehensive and unified study of the phonon properties of US. The calculated phonon dispersion curves of US using the present model agree reasonably well with the experimental data. We also report the specific heat variations, two phonon IR/Raman spectra, and anharmonic properties of US.

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I. INTRODUCTION

The study of the lattice dynamics of uranium monochalcogenides (US, USe, and UTe) has been the object of considerable and continuing interest in solid state physics. Their partially ionic nature is characterized by high energy gaps, high dielectric constants and large negative-ion electronic polarizabilities ($\alpha^-$). Because of their unique physical properties and the degeneracy in their optical vibration frequencies at the zone center (Γ-point), these crystals have always offered fascinating and challenging fields for both theoretical and experimental workers. This fact is self-evident from the development of numerous phenomenological models [1–3] for predicting the available experimental data on phonon dispersion [4, 5] and specific heats [6–8].

The rigid ion model (RIM) and the shell model have been fitted and employed by Jackman et al. [4] to determine the phonon dispersion relations of uranium compounds, but the models exhibit a common lack of agreement in the neighbourhood of the X-point in the Brillouin zone. Furthermore, these models, RIM and SM, fail also to explain the large Cauchy violation in the elastic constants for these compounds.

In an attempt to account for this, Jha and Sanyal [1] used a lattice dynamical model (TRIM) which includes threebody forces in the framework of the rigidion model (RIM). Their model (TRIM) explained the degeneracy of the optical branches satisfactorily but failed to explain the anomalies observed at the X-point and along the [q q 0] direction. For better results, Jha and Sanyal [3] used a breathing shell model (BSM). The results obtained by using this model are better than those by their previous models, but are still not entirely satisfactory; a failure can be seen for the optical frequencies particularly at the
L-point and for the TA branch along \([q 0 0]\) for US. These facts emphasize the necessity for other phenomenological models which may successfully describe the phonon properties of US. Motivated by this remark the present authors have reformulated TSM and developed a model (vTSM) which includes three body interactions and van der Waals interactions in the framework of the polarizable rigid shell model for both ions. The present model vTSM is used to study the phonon properties of US.

II. THEORY

The general formalism of vTSM can be derived from the crystal potential, whose relevant expression per unit cell is given by

\[
\Phi = \Phi^C + \Phi^R + \Phi^{TBI} + \Phi^{VWI},
\]

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

Using the crystal expression (1) and introducing the effect of vWI and TBI, the secular determinant

\[
\begin{vmatrix}
D(q) - \omega^2 M \nu
\end{vmatrix} = 0,
\]

is used for the frequency determination. Here \(D(q)\) is the \((6 \times 6)\) dynamical matrix given by

\[
D(q) = (R + Z_m C' Z_m) - (T + Z_m C' Y_m) \times (S + K + Y_m C' Y_m)^{-1} \times (T^T + Y_m C' Z_m)
\]

The number of adjustable parameters has been largely reduced by considering all the short-range interactions to act only through the shells. This assumption leads to \(R = T = S\). \(C'\) is the modified long-range interaction matrix given by

\[
C' = C + (Z_m^{-2} Z r_0 f_0) Y,
\]

and the elements of the short-range matrix \(R\), including the first and second-neighbour interactions have been represented by

\[
R_{\alpha\beta}(kk') = [\Phi_{\alpha\alpha}(kk)]_0 + \sum \frac{Z^2 e^2}{2u} \left\{ \frac{X_\alpha X_\beta}{r^2} (A_{12} - B_{12}) + \delta_{\alpha\beta} B_{12} \right\} \\
+ \frac{Z^2 e^2}{4u} \left\{ \frac{X_\alpha X_\beta}{r^2} (A_{11} + A_{22} - B_{11} - B_{22}) + \delta_{\alpha\beta} (B_{11} + B_{22}) \right\} \\
\times \exp \{i\mathbf{q} \cdot (l'k' - l'k)\},
\]
where the first term shows a “self-interaction”, \( v \) is the volume of the unit cell, \( \delta_{\alpha\beta} \) is the Kronecker delta, and \((A_{12}, B_{12})\) and \((A_{11}, A_{22}, B_{11}, B_{22})\) are the short-range parameters for the nearest neighbours and the next nearest neighbours, respectively. These are defined by

\[
B_{12} = \frac{4r_0^2}{e^2} \left[ \frac{d}{dr} \Phi_1^{(R)} (r) \right]_{r=r_0}, \quad A_{12} = \frac{4r_0^3}{e^2} \left[ \frac{d^2}{dr^2} \Phi_1^{(R)} (r) \right]_{r=r_0}, \quad (6)
\]

\[
\sqrt{2}(B_{11} + B_{22}) = \frac{4 (r_0 \sqrt{2})^2}{e^2} \left[ \frac{d}{dr} \Phi_2^{(R)} (r) \right]_{r=r_0 \sqrt{2}},
\]

\[
\sqrt{2}(A_{11} + A_{22}) = \frac{4 (r_0 \sqrt{2})^3}{e^2} \left[ \frac{d^2}{dr^2} \Phi_2^{(R)} (r) \right]_{r=r_0 \sqrt{2}}, \quad (7)
\]

where, \( \Phi_1^{(R)} (r) \) and \( \Phi_2^{(R)} (r) \) are the overlap potentials between the nearest neighbours and the next nearest neighbours, respectively.

The various elements of the \( R \) matrix derived from Eq. (5) are

\[
R_{\alpha\alpha} (kk) = R_0 + \frac{Z^2 e^2}{v} \left[ (A_{11} + A_{22}) + 2 (B_{11} + B_{22}) - \frac{A_{11} + A_{22} + B_{11} + B_{22}}{2} \right. \\
\times \cos \pi q_\alpha (\cos \pi q_\beta + \cos \pi q_\gamma) - (B_{11} + B_{22}) \cos \pi q_\beta \cos \pi q_\gamma \right] \quad (8)
\]

\[
R_{\alpha\alpha} (kk) = \frac{Z^2 e^2}{v} \left[ A_{12} \cos \pi q_\alpha + B_{12} (\cos \pi q_\beta + \cos \pi q_\gamma) \right] = R_1, \quad (9)
\]

\[
R_{\alpha\beta} (kk) = \frac{Z^2 e^2}{v} \left[ A_{11} + A_{22} - B_{11} - B_{22} - \sin \pi q_\alpha \sin \pi q_\beta \right], \quad (10)
\]

\[
R_{\alpha\beta} (kk') = 0, \quad (11)
\]

with

\[
R_0 = [R_{\alpha\alpha} (kk)]_{q-0} = -\left[ R_{\alpha\alpha} (kk') \right]_{q-0} = \frac{Z^2 e^2}{v} (A_{12} + 2B_{12}). \quad (12)
\]

These expressions are the same as those already given by Cowley and Okazaki [9]. The expressions derived for the elastic constants from equation (1) corresponding to the present model are obtained as

\[
\frac{4r_0^4}{e^2} C_{11} = \left[ -5.112 \xi^2 + A_{12} + \frac{1}{2} (A_{11} + A_{22}) + \frac{1}{2} (B_{11} + B_{22}) + 9.3204 \xi^2 \right], \quad (13)
\]
TABLE I: Input data and model parameters for US.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
<th>Ref.</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$ ($10^{12}$ dyne/cm$^2$)</td>
<td>2.59</td>
<td>[3]</td>
<td>$Z_{m}^2$</td>
<td>2.2470</td>
</tr>
<tr>
<td>$C_{12}$ ($10^{12}$ dyne/cm$^2$)</td>
<td>0.02</td>
<td>[3]</td>
<td>$r_0 f'_0$</td>
<td>-0.1056</td>
</tr>
<tr>
<td>$C_{44}$ ($10^{12}$ dyne/cm$^2$)</td>
<td>0.22</td>
<td>[3]</td>
<td>$A_{12}$</td>
<td>40.3751</td>
</tr>
<tr>
<td>$\nu_{LO}(\Gamma) = \nu_{TO}(\Gamma)$ (THz)</td>
<td>9.50</td>
<td>[4]</td>
<td>$B_{12}$</td>
<td>-3.0981</td>
</tr>
<tr>
<td>$\nu_{LO}(L)$ (THz)</td>
<td>9.32</td>
<td>[4]</td>
<td>$A_{11}$</td>
<td>-14.2253</td>
</tr>
<tr>
<td>$\nu_{TO}(L)$ (THz)</td>
<td>9.31</td>
<td>[4]</td>
<td>$B_{11}$</td>
<td>26.3959</td>
</tr>
<tr>
<td>$\nu_{LA}(L)$ (THz)</td>
<td>3.09</td>
<td>[4]</td>
<td>$A_{22}$</td>
<td>10.8615</td>
</tr>
<tr>
<td>$r_o (10^{-8}$ cm)</td>
<td>2.75</td>
<td>[3]</td>
<td>$d_1$</td>
<td>0.2125</td>
</tr>
<tr>
<td>$\alpha_1 (10^{-24}$ cm$^3$)</td>
<td>0.40</td>
<td>[3]</td>
<td>$d_2$</td>
<td>1.7114</td>
</tr>
<tr>
<td>$\alpha_2 (10^{-24}$ cm$^3$)</td>
<td>5.50</td>
<td>[3]</td>
<td>$Y_1$</td>
<td>-4.1530</td>
</tr>
<tr>
<td>$C_{++} (10^{-60}$ erg cm$^6$)</td>
<td>1428</td>
<td>[12]</td>
<td>$Y_2$</td>
<td>-7.0894</td>
</tr>
<tr>
<td>$C_{--} (10^{-60}$ erg cm$^6$)</td>
<td>481</td>
<td>[12]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\frac{4r_0^4}{e^2} C_{12} = \left[ 2.226\xi^2 - B_{12} + \frac{1}{4} (A_{11} + A_{22}) - \frac{5}{4} (B_{11} + B_{22}) + 9.3204\xi'^2 \right].
\]

\[
\frac{4r_0^4}{e^2} C_{44} = \left[ 2.556\xi^2 + B_{12} + \frac{1}{4} (A_{11} + A_{22}) + \frac{3}{4} (B_{11} + B_{22}) \right].
\]

In view of the equilibrium condition, \([(d\Phi/dr)_0 = 0] \text{ or} \n B_{11} + B_{22} + B_{12} = -1.165\xi^2 ,
\]

where

\[
\xi = \pm \sqrt{\left( 1 + \frac{12 f(r)}{Z} \right)_0} \quad \text{and} \quad \xi' = \pm \sqrt{\left( \frac{r}{Z} \cdot \frac{df}{dr} \right)_0}
\]

The term $f(r)$ is a function dependent on the overlap integrals of the electron wavefunctions, and the subscript zero on the brackets indicates the equilibrium values of the quantities inside. The expression (15) can now be written in the form

\[
\frac{4r_0^4}{e^2} C_{44} = \left[ 1.391\xi^2 + \frac{A_{22} - B_{22}}{4} \right].
\]

As $C_{44}$ is a very small quantity in the present case, the calculated value of \( \left( 4r_0^4/e^2 \right) C_{44} - 1.391\xi'^2 \) is found to be a negative quantity so that \( A_{22} - B_{22} \) is negative. This suggests that these terms belong to an attractive interaction and possibly arise due to van der Waals energy. The van der Waals energy converges fast but the overlap repulsion converges much.
faster. Therefore, the overlap repulsion is effective only up to the first neighbour and the van der Waals attraction up to the second neighbour.

By solving the secular equation (2) along the \([q 0 0]\) direction and subjecting the short and long-range coupling coefficients to the long-wavelength limit \(q \rightarrow 0\), two distinct optical vibration frequencies are obtained as

\[
(\mu \omega_L^2)_{q=0} = R'_0 + \frac{(Z'e)^2}{v f_L} \cdot \frac{8\pi}{3} (\xi^2 + 6\xi'^2),
\]

\[
(\mu \omega_T^2)_{q=0} = R'_0 - \frac{(Z'e)^2}{v f_T} \cdot \frac{4\pi}{3} \cdot \xi^2,
\]

where the abbreviations stand for

\[
R'_0 = R_0 - e^2 \left( \frac{d_1^2}{\alpha_1} + \frac{d_2^2}{\alpha_2} \right), \quad Z' = Z_m + d_1 - d_2,
\]

\[
f_L = 1 + \left( \frac{\alpha_1 + \alpha_2}{v} \right) \cdot \frac{8\pi}{3} (\xi^2 + 6\xi'^2),
\]

\[
f_T = 1 - \left( \frac{\alpha_1 + \alpha_2}{v} \right) \cdot \frac{4\pi}{3} \xi^2, \quad \text{and} \quad \alpha = \alpha_1 + \alpha_2;
\]

but the expressions (19) and (20) reduced to the following equation as \(\omega_L = \omega_T\) for the present system of solids:

\[
\frac{8\pi (Z'e)^2}{3} \frac{v}{v} \left( \frac{\xi^2 + 6\xi'^2}{f_L} + \frac{\xi^2}{2f_T} \right) = 0.
\]

### III. RESULTS AND DISCUSSION

Our 12 model parameters have been calculated by using the interatomic separation \((r_0)\), the elastic constants \((C_{11}, C_{12}, \text{and } C_{44})\), the frequencies \(\nu_{LO}(\Gamma) = \nu_{TO}(\Gamma), \nu_{LO}(L), \nu_{TO}(L), \nu_{LA}(L), \text{and } \nu_{TA}(L)\), and the van der Waals coefficients \((C_{++}, C_{--})\). The input data along with the model parameters are given in Table I for US. These model parameters are used to compute the phonon spectra for the allowed 48 non-equivalent wave vectors in the first Brillouin zone. The frequencies along the symmetry directions have been plotted against the wave vector to obtain the phonon dispersion curves (PDC).

The calculated PDC along with the experimental values has been presented in Fig. 1. The phonon dispersion curves show that the inclusion of van der Waals interactions has improved the agreement between the experiments and our results. In addition, if we compare
### TABLE II: Assignments of two-phonon Raman and Infra-red peaks for US.

<table>
<thead>
<tr>
<th>CDS Peaks (cm$^{-1}$)</th>
<th>Raman Active</th>
<th>Infra-red Active</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present study</td>
<td>Present study</td>
</tr>
<tr>
<td></td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
</tr>
<tr>
<td>75</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>110</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>150–160</td>
<td>154 LA+TA (X)</td>
<td>152</td>
</tr>
<tr>
<td></td>
<td>162 2LA (X)</td>
<td>164</td>
</tr>
<tr>
<td></td>
<td>164 LA+TA (∆)</td>
<td>160</td>
</tr>
<tr>
<td>200</td>
<td>202 2TA (L)</td>
<td>200</td>
</tr>
<tr>
<td>240</td>
<td>238 LO–LA (X)</td>
<td>238</td>
</tr>
<tr>
<td>373</td>
<td>376 TO+TA (X)</td>
<td>373</td>
</tr>
<tr>
<td></td>
<td>377 TO+TA (∆)</td>
<td>374</td>
</tr>
<tr>
<td>410</td>
<td>-</td>
<td>412 TO+TA (L)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>LO+TA (L)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>TO+LA (L)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>LO+LA (L)</td>
</tr>
<tr>
<td>610</td>
<td>606 2TO (X)</td>
<td>606</td>
</tr>
<tr>
<td></td>
<td>612 2TO (∆)</td>
<td>614</td>
</tr>
<tr>
<td></td>
<td>629 LO+TO (∆)</td>
<td>629</td>
</tr>
<tr>
<td></td>
<td>634 2TO (Γ)</td>
<td>634</td>
</tr>
</tbody>
</table>

**FIG. 1:** Phonon dispersion curves for US.
TABLE III: Third and fourth order elastic constants (in units $10^{12}$ dyne/cm$^2$) for US.

<table>
<thead>
<tr>
<th>Property</th>
<th>Values</th>
<th>Property</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{111}$</td>
<td>766.1754</td>
<td>$C_{1122}$</td>
<td>2.8366</td>
</tr>
<tr>
<td>$C_{112}$</td>
<td>$-0.4700$</td>
<td>$C_{1266}$</td>
<td>3.2340</td>
</tr>
<tr>
<td>$C_{166}$</td>
<td>$-0.7185$</td>
<td>$C_{4444}$</td>
<td>2.9866</td>
</tr>
<tr>
<td>$C_{123}$</td>
<td>0.4414</td>
<td>$C_{1123}$</td>
<td>$-1.1762$</td>
</tr>
<tr>
<td>$C_{144}$</td>
<td>0.5608</td>
<td>$C_{1144}$</td>
<td>$-1.5969$</td>
</tr>
<tr>
<td>$C_{456}$</td>
<td>0.6205</td>
<td>$C_{1244}$</td>
<td>$-1.3572$</td>
</tr>
<tr>
<td>$C_{1111}$</td>
<td>994.1358</td>
<td>$C_{1456}$</td>
<td>$-1.5647$</td>
</tr>
<tr>
<td>$C_{1112}$</td>
<td>0.6695</td>
<td>$C_{4456}$</td>
<td>$-1.2827$</td>
</tr>
<tr>
<td>$C_{1166}$</td>
<td>2.2831</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

these results with those determined by using TRIM [1], it is evident that the three body force rigid ion model has yielded generally poor agreement with experimental data along the [q q 0] and [q q 0] directions. The 9-parameter BSM [3] has explained optical frequencies in almost all the symmetry directions but failed to explain the acoustic frequencies along the [q 0 0] and at the L point. The predictions of the phonon dispersion curves from vTSM may be considered more satisfactory than those achieved from TRIM [1] and BSM [3]. The inclusion of vWI with TBI has influenced both the LO and TO branches much more than the acoustic branches. Both optical and acoustic branches in all symmetry directions have been excellently reproduced by the present model.

The physical properties IR/Raman spectra and the specific heat variations are sensitive to the higher and lower sides of the frequency spectra, hence to test any model these properties play an important role. We have plotted the variation of the specific heat with the square of temperature. It is evident from Fig. 2 that our results are in good agreement with the measurement data [6] and are generally better than those obtained by using the BSM [3]. The small deviation at higher temperature might be mainly due to the anharmonicity involved in the lattice vibrations.

In order to interpret the second order infrared and Raman spectra we have employed the combined density of states approach [10]. The computed combined density of states curves have been shown in Fig. 3. A comparison of our CDS peaks with their assignments from the two phonon IR/Raman spectra with the help of neutron data [4] has been given in Table II. The basic aim of the detailed study of the combined density of states is to correlate the neutron and optical experimental results for US.

The anharmonic properties give valuable information about the binding forces between the constituents of a crystal, so we have studied also these properties. The expressions for the third order and fourth order elastic constants and the pressure derivatives of the second order elastic constants (SOEC) derived by us corresponding to the three-body lattice energy are similar to those derived by Puri, Garg, and Verma [11]. The third order and fourth order elastic constants and the pressure derivatives of the SOE and TOE constants are presented in Table III–IV, respectively. Since no experimental results on these
FIG. 2: Specific heat as a function of $T^2$.

TABLE IV: Values of pressure derivatives of SOE and TOE constants for US.

<table>
<thead>
<tr>
<th>Property</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$dK'/dP$</td>
<td>6.5033</td>
</tr>
<tr>
<td>$dS'/dP$</td>
<td>8.0967</td>
</tr>
<tr>
<td>$dC_{44}'/dP$</td>
<td>$-1.0228$</td>
</tr>
<tr>
<td>$dC_{111}'/dP$</td>
<td>$-1249.4812$</td>
</tr>
<tr>
<td>$dC_{112}'/dP$</td>
<td>$-1.3497$</td>
</tr>
<tr>
<td>$dC_{166}'/dP$</td>
<td>1.9836</td>
</tr>
<tr>
<td>$dC_{123}'/dP$</td>
<td>1.8381</td>
</tr>
<tr>
<td>$dC_{144}'/dP$</td>
<td>$-0.0005$</td>
</tr>
<tr>
<td>$dC_{456}'/dP$</td>
<td>2.0770</td>
</tr>
</tbody>
</table>

properties have been reported so far it is not possible to comment on them.

IV. CONCLUSION

The overall excellent agreement between the present results and experimental data for the phonon properties of US leads to the conclusion that the van der Waals interactions
play an important role in the lattice dynamics of US. The discussions on phonon dispersion curves, specific heat variations, and the combined density of states in the previous section clearly prove that vTSM predictions are reasonably better than those predicted by the earlier models [1–3]. Our extensive study of anharmonic properties will be quite helpful for experimental workers when analyzing their results in future. To summarize, we can say that the contribution of the van der Waals and three body interactions in the lattice dynamics of US is significant, and our model vTSM is reasonably an appropriate model for the complete study of the phonon properties of US.

Acknowledgments

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References