



## Many Body Interactions on Lattice Vibrational Properties of Plutonium Arsenides†

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Many body interactions, which includes the effect of van der Waals interactions (vWI) and three body interactions in the framework of rigid shell model, has been employed to study the lattice dynamics of plutonium arsenides. It is assumed 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. Because of *f-d* hybridization, the large LO-TO phonon splitting at zone centre predicted. The agreement between our predictions and available neutron 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 of plutonium arsenides.

**Key Words:** Phonons, Lattice vibrational properties.

### INTRODUCTION

The study of phonon vibrational properties of plutonium arsenide (PuAs) is very interesting, crystallizing into rock-salt structure PuAs has a Fm3m, face-centered cubic with lattice parameter  $a_0 = 5.859 \text{ \AA}$  and orders ferromagnetically. Although several theoretical models have been used to predict the phonon dispersion curves (PDCs) of these solids but only with moderate success. After introducing anharmonic vibration in the many-body interactions, it is expected that a composite model taking both the effects into account will improve the discrepancies between theory and neutron data. The phonon dynamics of PuAs was studied by various theoretical workers with successively improved models<sup>1-3</sup>. Although this approach is better than other but without including van der Waals interactions the complete vibrational properties can not be investigated. In order to explain the lattice vibrational behaviour of plutonium arsenides better, we have employed a model which includes van der Waals interactions and three body interactions and short-range repulsion effective up to the second neighbors in the frame work of rigid shell model. The parameters of this model have been calculated by using measured values of inter-ionic distance ( $r_0$ ), elastic constants ( $C_{11}$ ,  $C_{12}$ ,  $C_{44}$ ), electronic polarizabilities ( $\alpha_1$ ,  $\alpha_2$ ) and frequencies along  $\Gamma$ , X, M and R symmetry directions. These model parameters have been used to compute the phonon spectra for the allowed 48-non-equivalent wave vectors in the first brillouin zone of NaCl structure.

### Lattice dynamical model

The shell model can be incorporated into the formalism of the dynamical matrix by writing separate equations of motion for the core and the shell. Because the mass of the shell is zero in the shell model, there is no separate  $m\omega^2$  for the shell. Instead, the shell instantaneously relaxes to its equilibrium position so that there is no restoring force on the shell. Thus the displacement of the shell is completely tied to the displacement of the cores and therefore there is not a separate solution for the shell. The contributions of the shells fold into an expanded dynamical matrix for the ionic cores and giving the same number of solutions as for models without ionic shells. There has been always a continuing effort to obtain accurate interatomic potential functions. The interaction potential energy function is generally used to study the crystalline properties of diatomic crystal. The total potential for the plutonium arsenides can be written as

$$\Phi = \Phi^C + \Phi^R + \Phi^{\text{TBI}} + \Phi^{\text{VWI}} \quad (1)$$

When first term  $\Phi^C$  is coulomb interaction potential and is long-range in nature, second term is  $\Phi^R$  short-range overlap repulsion potential, third term  $\Phi^{\text{TBI}}$  is three-body interactions potential and the last term is  $\Phi^{\text{VWI}}$  van der Waals interactions potential and owes its origin to the correlations of the electron motions in different atoms. We consider that van der Waals energy converges fast but the overlap repulsion converges much

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faster. Therefore, the overlap repulsion is effective only up to the first neighbor and the van der Waals attraction up to the second neighbors<sup>4,5</sup>.

Using the crystal potential expression (1) the equations of motion of two cores and two shells can be written as:

$$\omega^2 \underline{M} \underline{U} = (\underline{R} + \underline{Z}_m \underline{C}' \underline{Z}_m) \underline{U} + (\underline{T} + \underline{Z}_m \underline{C}' \underline{Y}_m) \underline{W} \quad (2)$$

$$\underline{O} = (\underline{T}' + \underline{Y}_m \underline{C}' \underline{Z}_m) \underline{U} + (\underline{S} + \underline{K} + \underline{Y}_m \underline{C}' \underline{Y}_m) \underline{W} \quad (3)$$

Here  $\underline{U}$  and  $\underline{W}$  are vectors describing the ionic displacements and deformations, respectively.  $\underline{Z}_m$  and  $\underline{Y}_m$  are diagonal matrices of modified ionic charges and shell charges, respectively. The elements of matrix  $\underline{Z}_m$  consists of the parameter  $Z_m$  giving the modified ionic charge.

$$Z_m = Z\xi = \pm Z\sqrt{1 + (n/Z)f_0} \quad (4)$$

This means that the ionic charge parameter ( $Z$ ) of rigid shell model gets modified by a factor  $\{1 + (12/Z)f_0\}$  for NaCl - structure.

The elimination of  $\underline{W}$  from eqns. 2 and 3 leads to the secular determinant:

$$|\underline{D}(\vec{q}) - \omega^2 \underline{M}| = 0 \quad (5)$$

Here  $\underline{D}(\vec{q})$  is the  $(6 \times 6)$  dynamical matrix given by

$$\underline{D}(\vec{q}) = (\underline{R}' + \underline{Z}_m \underline{C}' \underline{Z}_m) - (\underline{T} + \underline{Z}_m \underline{C}' \underline{Y}_m) \times (\underline{S} + \underline{K} + \underline{Y}_m \underline{C}' \underline{Y}_m)^{-1} (\underline{T}' + \underline{Y}_m \underline{C}' \underline{Z}_m) \quad (6)$$

The dynamical matrix, given by equation (5), is a matrix  $(6 \times 6)$  leading to six vibrational frequencies ( $\omega$ ) corresponding each phonon wave vector ( $\vec{q}$ ). For wave-vector ( $\vec{q}$ ) along the principal symmetry directions ( $\Gamma$ , X, L,  $\Delta$ ) for NaCl in the brillouin zone,  $\underline{D}(\vec{q})$  can be reduced to lower order ( $2 \times 2$ ) matrices which simplifies the computational work in solving the characteristic eqn. 6 and also the number of distinct branches of the dispersion relations get reduced because of the degeneracy.

## RESULTS AND DISCUSSION

**Phonon dispersion curves for plutonium arsenide:** The phonon dispersion relations have been computed by solving the secular equation for the six vibration frequencies corresponding to the phonon wave vectors ( $q$ ) along the principal symmetry direction  $[q00]$ ,  $[00q]$  and  $[qqq]$ . The phonon dispersion curves (Figure 1) have been obtained by plotting these vibration frequencies ( $\nu$ ) against the wave vector ( $q$ ) and following points are inferred from the careful analysis of phonon dispersion curves of plutonium arsenide. The dispersion of the longitudinal phonon exhibits oscillatory behaviour extending to the large wave vector transfer region. In contrast, the  $\nu$ - $q$  curves for transverse phonons the oscillatory behaviour seems quite insignificant for higher  $q$  value. This indicates that the transverse phonons undergo large thermal modulation than do the longitudinal phonon, due to the anharmonicity of atomic vibration at room temperature. The  $\nu$ - $q$  curves for transverse phonons attain maxima at a higher  $q$  value than the longitudinal phonon curves. Three body interactions have influenced LO and TO branches much more than the acoustic branches LA and TA in these halides. The main feature to note is that there is not a separation of optic and acoustic mode

frequencies across the range of wave vectors; this is because of the association of optical vibrations with electric moments. The transverse modes do indeed show a separation of the optic and acoustic modes but there is not a separation of LO and LA modes. Optical vibrations are important chiefly in the plutonium chalcogenides, owing to the strong electric moments associated with motion. Lattice vibrations with wave vector  $[q00]$  are showing LO modes have cations and anions moving in opposite directions parallel to  $[q00]$  and the TO modes have the cations and anions moving in opposite directions perpendicular to  $[q00]$ . At  $[000]$ , the both types of motion become exactly equivalent, in this case LO and TO frequencies would be equal. But as shifting from  $[000]$  to  $[q00]$ , the long-wavelength optic modes generate electric fields that are either parallel or perpendicular to the direction of propagation of the optic mode will have a significant effect on the frequency of the mode. It follows that  $\nu_{LO} > \nu_{TO}$ . This effect is known as LO/TO splitting, reflecting the fact at exactly zero wave vector the frequencies are the same.

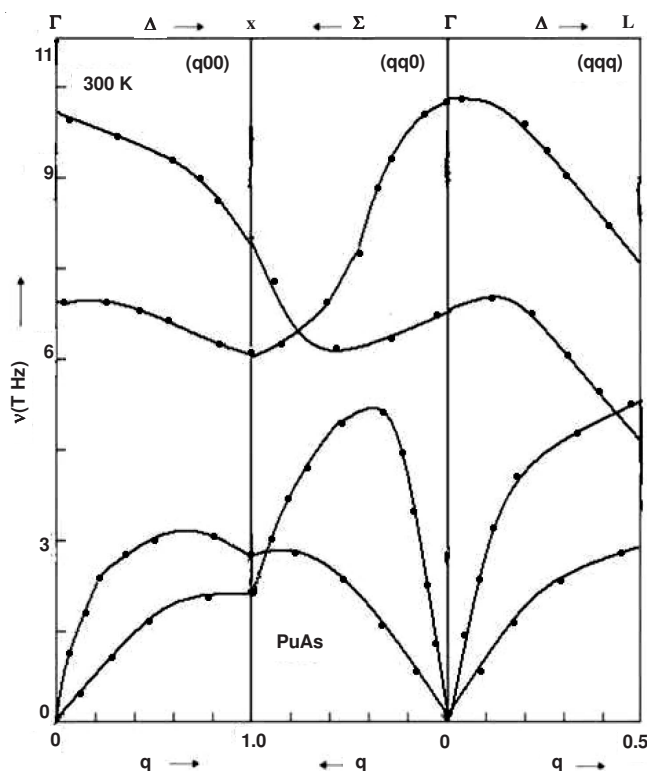


Fig. 1. Phonon dispersion curves of plutonium arsenide

**Two phonon IR/Raman spectra of plutonium arsenides:** Two-phonon processes are possible in both these classes of experiments. Such two-phonon processes give rise to a number of prominent subsidiary peaks in second-order infrared absorption and Raman scattering experiments distributed over a large frequency range. The two-phonon processes in ionic solids can be understood to result from two distinct effects: one due to second or higher order terms in the expression of dipole moments as a power series in ionic displacements and the other due to presence of third and higher order anharmonic terms in the lattice potential energy. We have studied the effect of second-order dipole moment term and the third order

anharmonic term on the infrared and Raman spectra of solids and these terms give rise to sum and difference modes of lattice vibration frequencies. The difference modes do not contribute to the absorption peaks since they are distributed over a large frequency interval. Therefore, the observed absorption peaks can be interpreted as being due to the sum modes or in other words due to consecutive emission or absorption of two phonons. However, both the absorption peaks in the infrared spectra and the peaks observed in the intensity versus frequency shifts in the Raman scattering experiments must correspond to the peaks in the two-phonon combined density of states  $N(\nu_i + \nu_j)$  plotted against  $(\nu_i + \nu_j)$ .

The combined density of states (CDS) can be computed from the lattice vibration frequencies by subjecting their sum to the following selection rules<sup>6</sup>.

(i) If one of the phonons corresponds to a wave-vector  $q_\alpha$  the other must correspond to  $-q_\alpha$ .

(ii) In solids where every atom (or ion) is at a center of inversion symmetry the two phonons must come from different branches of the spectrum.

In view of the first selection rule, the allowed overtones and combinations are  ${}^6C_0 + {}^6C_2$ . This leads to the existence of 21 sum modes corresponding to each phonon wave-vector. While the restriction imposed by the second rule excludes the possibility of  $({}^6C_0 =)$  6 overtones and allows only 15 ( $= {}^6C_2$ ) combinations to be possible. It is shown in the Fig. 2 that the second-order Raman spectrum contains both the overtones and the combinations while an infrared spectrum contains only the combinations. Thus, to analyze the data on second-order Raman spectra only first rule is sufficient while for correct description of infrared spectra both the rules are needed. The maxima in the absorption are closely associated with the maxima in the combined density of states such that the sharply defined maxima in the density of states correspond to sharper absorption peaks and less sharply defined maxima correspond to broader peaks. In general, it is found that the well defined peaks in combined density of states curves subject to both selection rules correspond to the combination modes of the second-order infrared spectra. While the combined density of states curves obtained from the first selection rule correspond to peaks both for combinations and overtones of the second-order Raman spectra. Thus, combined density of states curves may be regarded as a true representative of absorption spectra and not for Raman spectra. This is due to the fact that fine structure of Raman spectra being sensitive to the difference

modes remains explained in combined density of states approach.

**Debye temperatures variation:** The variation of the experimentally measured specific heats is compared with that computed from the phonon spectra. This comparison is usually done by plotting the Debye temperatures against the temperature. For calculating the exact variation of Debye temperatures we have used the Blackmann's<sup>7</sup> sampling technique. In this technique, the frequency spectrum is divided into a suitable number of equal intervals and the specific heat is expressed as a sum over Einstein functions corresponding to the mid point of each interval. Thus,

$$C_v = \frac{3\Re}{6000} \sum_{\nu} g(\nu)E(\nu)d\nu \quad (7)$$

where  $E(\nu)$  is the Einstein function,  $\Re$  is the gas constant and  $g(\nu)d\nu$  are the number of frequencies lying in the interval  $(\nu-d\nu/2)$  to  $(\nu+d\nu/2)$ . From the calculated specific heats at different temperatures,  $\Theta_D$  is calculated by means of standard tables. Thus  $(\Theta_D-T)$  curve is plotted (Fig. 3) and compared with the available experimental data. The specific heat at constant volume behaviour of the PuAs does not show any anomaly.

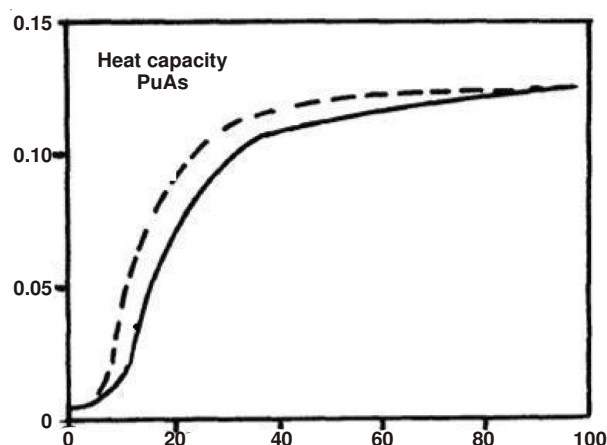


Fig. 3. Lattice specific heat of PuAs

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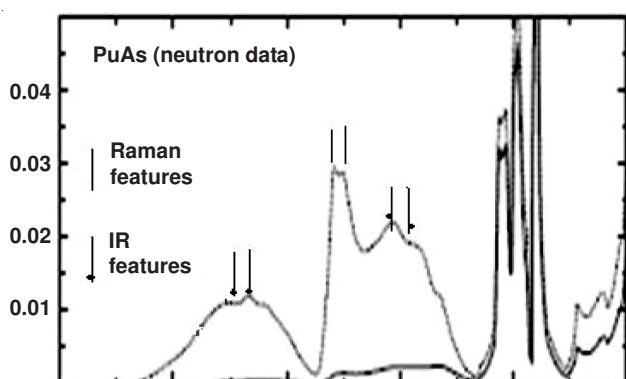


Fig. 2. Combined density of states curve for plutonium arsenide