

Lattice vibrational properties of uranium pnictides

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Abstract. Lattice vibrational properties of uranium pnictides have been studied using breathing shell model (BSM) which includes breathing motion of electrons of the U-atoms due to $f-d$ hybridization. The phonon dispersion curves of U-pnictides calculated from the present model agree reasonably well with the measured data. A comparison has been made between BSM and our results reported earlier obtained from three-body force rigid ion model to reveal the importance of the short-range electron-phonon interactions in these compounds. We also report, for the first time, the two phonon density of states and specific heat for these compounds.

Keywords. Lattice vibrational; phonons; dispersion curves; breathing shell model; dynamical matrix.

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1. Introduction

The uranium compounds (UX, $X = N, P, As, Sb, S, Se, Te$) crystallize in rocksalt structure and show wide variety of anomalous behaviour as far as their electronic [1–2], elastic [3–6], magnetic [7] and phonon [8–13] properties are concerned. The phonon properties for these compounds have been studied using rigid ion (RIM) and shell models (SM) by Jackman *et al* [8], three-body force rigid ion model (TRIM) [9] and three-body force shell model (TSM) [10]. Amongst these models, RIM and SM are two-body in nature and fail to explain Cauchy violation ($C_{12} \neq C_{44}$) in the elastic constants. The elastic constant C_{12} for almost all the U-compounds has very small magnitude. Also, the degeneracy in the optical branches along principal symmetry directions and peculiar acoustic behaviour emphasize the necessity of the inclusion of electron-phonon interactions phenomenologically in the dynamical matrix for predicting the anomalous phonon properties in these compounds.

In a recent paper we have considered the many-body interactions arising from charge transfer effects between nearest neighbour ions in the framework of TRIM [9]. The TRIM could explain the gross features of the phonon dispersion curves (PDC), particularly the degeneracy of the optical branches but failed to explain the anomalies observed in the acoustic branches. In addition, this model also neglects the electron ion interactions e.g., electronic polarizabilities which might influence these modes at X-point. The electronic structure and symmetry considerations of the UX compounds depict that inclusion of the breathing motion of the electron shells leading to charge density deformations at U-atom site in the equation of motion might improve our understanding of phonon anomalies in U-compounds. The use

of such an approach has also been emphasized earlier by several workers to explain their phonon properties [14–16].

In the present paper we study the lattice vibrational properties such as phonon dispersion curves, BSM [17]. The BSM considers phenomenologically the breathing motion of electron shells resulting into charge density deformation due to $f-d$ hybridization. This model has already been used to study the phonon properties in intermediate valence compounds by Kress *et al* [18] and uranium chalcogenides by us [11].

2. Theory

The breathing shell model considers phenomenologically the short range electron-phonon interactions in terms of electron shell deformations. Depending upon symmetry, it includes dipolar, quadrupolar and breathing deformabilities of the electron shells of the polarizable ions. A detailed review of this model can be found elsewhere [17, 19].

The dynamical matrix corresponding to BSM is

$$D(q) = (R' + ZCZ) - (R' + ZCY)(R' + K + YCY)^{-1}(R' + YCZ) \quad (1)$$

where

$$R' = (R - QH^{-1}Q^+) \quad (2)$$

Here C and R are the Coulomb and short-range repulsive interaction matrices. Q is a (6×2) matrix representing the interactions between the ion displacement and breathing mode variables, 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 force constants and shell charges, respectively.

The present version of BSM has altogether eight parameters, which can be determined from elastic, dielectric and zone centre phonon properties. We have assumed $Y_1 = Y_2 = Y$ to minimize the number of parameters. The input data and model parameters are listed in tables 1 and 2, respectively.

Table 1. Input constants for uranium pnictides [8]. Elastic constants are in 10^{12} dyne/cm², lattice parameters in Å, frequencies are in THz and polarizabilities in Å³.

Parameters	UP	UAs	USb
a	5.590	5.779	5.489
C_{11}	—	2.50 ± 0.1	1.60 ± 0.1
C_{12}	—	0.10 ± 0.05	0.07 ± 0.15
C_{44}	—	0.26 ± 0.05	0.20 ± 0.10
$\nu_{TO}(\Gamma)$	9.200	5.990	4.700
α_1	0.550	0.500	0.430
α_2	7.250	7.500	8.200

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Table 2. Model parameters for uranium pnictides (for BSM). All are in units of $e^2/2V$ except Y which is in units of e .

Parameters	UP ^a	UAs	USb
A ₁₂	34.109	31.261	23.813
B ₁₂	5.054	4.804	4.150
A ₁₁	2.139	3.142	5.390
B ₁₁	-2.237	-1.988	-1.541
B ₂₂	0.800	0.933	1.205
Y	-26.610	-22.640	-12.220
G ₁ ($\times 10^2$)	695.770	575.235	207.328
G ₂ ($\times 10$)	423.570	288.754	106.206

^aValues obtained from linear interpolation.

3. Results and discussion

The calculated PDC for U-pnictides (UP, UAs and USb) have been plotted in figures 1–3 and compared with earlier calculated TRIM results [9] and neutron scattering data [8]. In calculating these curves we have, however, not attempted a least square fit to the phonon data but obtained them from the parameters which are physical in nature and derived from crystal properties.

The calculated PDC for UP from TRIM and BSM are plotted in figures 1(a) and (b). In the absence of sufficient measured properties, the force constants for UP are obtained from a linear interpolation of the results of other two members (UAs and USb) of this group. The theoretical results on PDC for UP have also been obtained by Jackman *et al* [8] from RIM using similar method. A close scrutiny of these two results reveals that BSM predicts non-degenerate LO and TO frequencies at X-point, which is not observed in the RIM results [8]. Also, the BSM predicts the LA and TA branches along (qqq) to be nearly degenerate, a feature shown by other members of this family, while the TRIM shows a smooth dispersion of these two branches similar to the RIM results. In the absence of any experimental data, relative merit of either of the model calculations cannot be judged at this moment. We believe that these results will be quite useful to the experimentalists when the PDC for UP are measured.

The PDC for UAs and USb are plotted in figures 2 and 3 from BSM and TRIM and compared with experimental results [8, 13]. The LA and TA branches along ($q00$) direction for these compounds have been reproduced fairly well by both the models, while a marked disagreement is observed at X-point, particularly in TRIM. Both the models predict degeneracy in the optical branches similar to experiment. All the phonon modes along all the symmetry directions for UAs are explained satisfactorily by BSM, even without any fitting. In UAs, it seems that the BSM predictions are better than those of TRIM along (qqq) direction.

The PDC for USb, plotted in figure 3, reveals that the acoustic modes in all symmetry directions are satisfactorily reproduced by both TRIM and BSM. Large difference between LO and TO along ($qq0$) direction is a common feature shown by both the models. The difference is maximum at (0.5, 0.5, 0.0). A similar situation is also observed from the RIM fit to the neutron scattering results [8]. The TRIM prediction of large splitting between LO and TO frequencies for USb at L-point

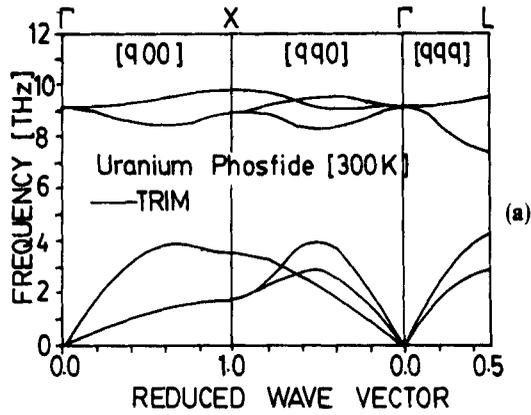


Figure 1(a). Phonon dispersion curves for UP using BSM.

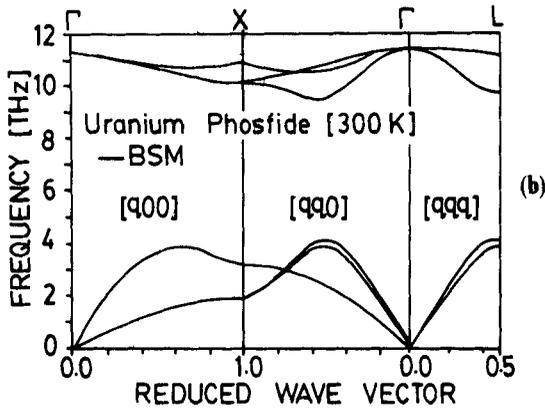


Figure 1(b). Same as in figure 1(a) for UP using TRIM.

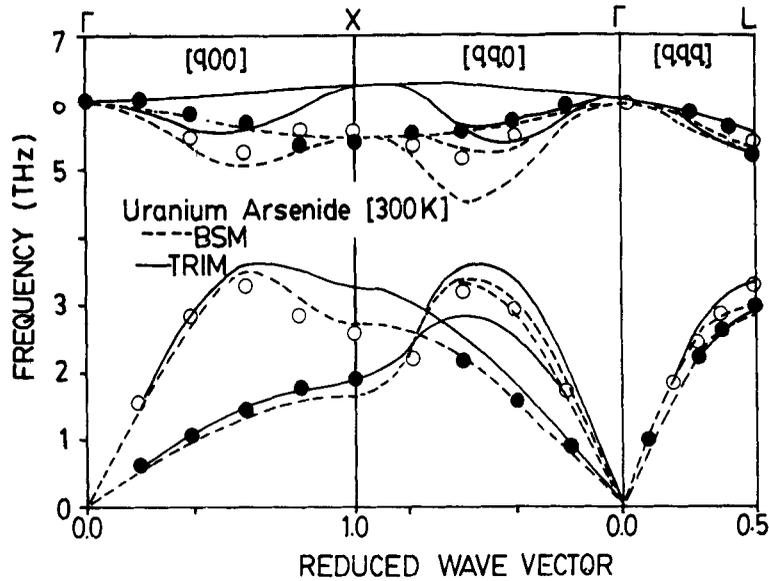


Figure 2. Same as in figure 1 for UAs. Experimental points are taken from Jackman *et al* [8] and Stirling *et al* [13].

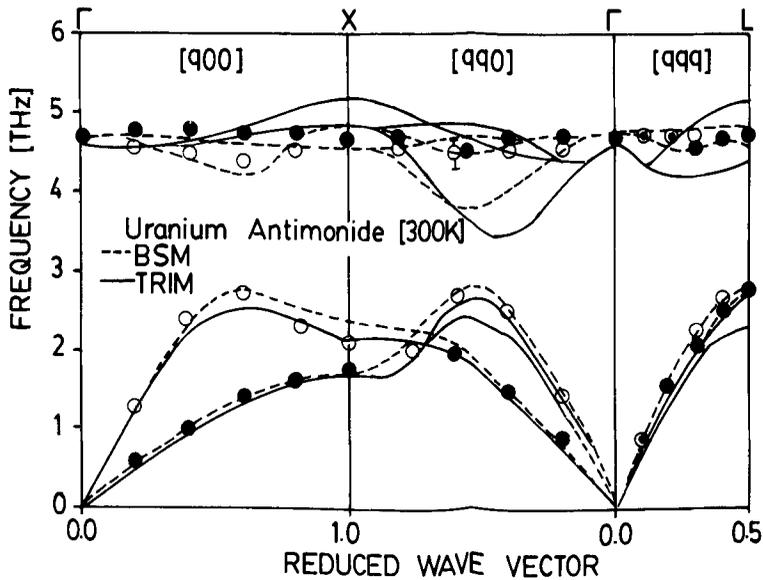


Figure 3. Same as in figure 1 for USb. Experimental points are taken from Jackman *et al* [8] and Stirling *et al* [13].

reveals its failure to take proper account of short-range interactions. In general, the optic branches are less satisfactorily explained by TRIM than BSM for uranium pnictides.

The lattice vibrations in uranium pnictides can be understood convincingly by analyzing the force constants derived from the present model (BSM). We present them in table 2. The salient feature of dominance of U-X (X = P, As, Sb) force constants in all U-pnictides, as is observed from RIM fit [8] has been fairly reproduced by BSM. The U-X force constants derived from BSM are nearly constant across the series. The relatively smaller magnitudes of second neighbour force constants are, to a greater extent, influenced by small magnitudes of bulk modulus of these compounds. Across the pnictide series, our calculated force constants show a similar trend of variation, similar to what is observed in RIM fit to the phonon data.

Finally, in this paper we have presented the results of a systematic study of a few phonon properties of the uranium pnictides. The calculated results point out that the phonon anomalies in these compounds, in general, originate from the breathing motion of the electron shells of uranium ions. The breathing shell model satisfactorily reproduces the gross features of the PDC. These predictions reveal that the polarizabilities of the ions are important and must be included in a realistic model approach. In addition, the short-range deformations due to breathing motion of the electron shells of U-ion contribute significantly to the peculiar phonon dispersion in uranium pnictides.

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