

Phonon properties of rare earth ytterbium pnictides

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Abstract. We report for the first time the complete phonon dispersion curves for the ytterbium pnictide compounds (YbN, YbP and YbAs) using a breathing shell model to establish their predominant ionic nature. The calculated results also show that this group of rare earth compounds does not show any elastic and phonon anomalies which are the characteristic features of other rare earth compounds. We emphasize the need for further Raman and neutron scattering measurements.

Keywords. Phonon dispersion curves; density of states; rare earth; intermediate valence compounds.

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1. Introduction

Over the last couple of decades, rare earth (RE) pnictides and chalcogenides have evoked considerable interest because of their diverse electronic, magnetic, optical and phonon properties [1–7]. The special feature of these materials is the valence fluctuation due to strong correlation among the ionic radius, the valence and the $4f$ occupation number. The latter is nominally integral for these core level type of localized states. However, a time-averaged non-integral $4f$ occupation number occurs in mixed valence compounds due to the degeneracy of two $4f$ configurations, e.g. $4f^n(\text{RE}^{2+})$ and $4f^{n-1}5d^1(\text{RE}^{3+})$. These two configurations can hybridize into a new ground state, which can be perturbed by either temperature or pressure. Some of these solids for which phonon properties have been studied so far are SmS, $\text{Sm}_x\text{Y}_{1-x}\text{S}$, TmSe, Tm_xSe [8–14]. All these studies have revealed that there is a strong electron phonon coupling at the RE ion site due to $4f$ – $5d$ hybridization giving rise to anomalies in their phonon dispersion curves [12–14]. Both semiconducting and metallic behaviour have been observed in this wide class of materials. Detailed reviews of phonon anomalies in RE compounds and intermediate valence compounds (IVC) materials can be found in refs [1 and 2].

Recently the elastic, optical and phonon properties of another class of RE-compounds, namely ytterbium pnictides (YbN, YbAs and YbP) have been reported by ETH, Zurich group [15–16]. These authors have measured for the first time the elastic constants using Brillouin scattering and surface acoustic wave (SAW) technique [15] and optical and phonon properties using reflectivity measurements and Raman spectroscopy [16] for large single crystals of RE-pnictide compounds. They have established that these compounds are self compensated semi metals with an indirect overlap of p and d bands. The metallic nature, however, arises because of non-stoichiometric nature of the crystals, a behaviour more prominent in YbN, in comparison to YbAs

and YbP. These authors [15,16] have also emphasized that this group of RE-compounds are weakly intermediate valent (or moderate Kondo systems) with semi metallic nature.

While many more investigations are to be carried out to establish the physical properties of the Yb-pnictides, in the present paper we focus on the elastic and phonon properties of these compounds only. An inspection of the measured elastic constants [15] reveals that none of these materials show anomalies in their elastic properties, as are observed in $\text{Sm}_x\text{Y}_{1-x}\text{S}$ [14], YS [17], TmSe [13, 14] and some of the uranium pnictides and chalcogenides [18, 19]. Here, by elastic anomalies, we primarily refer to the negative magnitudes of Poisson ratio and C_{12} , which are the clear indications of valency fluctuation [2, 19, 20]. On the contrary, the elastic properties are quite similar to those of RE Europium chalcogenides (EuX , $X = \text{O, S, Se, Te}$) which do not exhibit valency fluctuation [21, 22].

On the other hand not much can be concluded about metallic and semimetallic nature from the Raman measurements [16] on the optical and phonon properties of these materials. However complete measurements on the phonon dispersion curves by the neutron scattering experiments can lead to some significant results. Thus, it is the juncture to calculate the complete phonon dispersion curves of these compounds with the help of the measured informations provided in refs [15, 16] and using suitable theoretical model in order to establish further the physical properties of this group of compounds. We briefly outline the theory in § 2 and present our calculated results in § 3.

2. The theoretical model

In the absence of any measured data on the phonon dispersion curves, except the $\omega_{\text{TO}}(\Gamma)$, it is difficult to choose a suitable model to predict them. In selecting the present lattice dynamical model (e.g. breathing shell model), we find the following arguments in our favour: (i) the authors in refs [15, 16] have mentioned that the Yb-pnictides are semi-metallic in nature, and therefore a LO-TO splitting is expected. In this respect we expect there will be no anomalous phonon features in PDC, and the PDC will be somewhat similar to those of SmS , rather than TmSe [12–14]. (ii) The measured elastic constants [15] for Yb-pnictides do not exhibit anomalous behaviour, except that C_{12} - C_{44} in YbN is negative while it is positive in YbP and YbAs . Therefore pronounced metallic nature, as is observed in U-pnictides and U-chalcogenides [18, 19] is expected to be absent. In view of the above discussion, we have chosen the breathing shell model (BSM) which has been found extremely successful in explaining the phonon anomalies in a wide class of rare earth (RE) compounds [23, 24]. The general theory of BSM considers the breathing motion of the electron shells with respect to the core of the RE-ion in the equations of motion [25].

In the adiabatic approximation equations of motion corresponding to BSM are given by

$$\begin{aligned}\omega^2\mathbf{M}\mathbf{U} &= (\mathbf{R} + \mathbf{Z}\mathbf{C}\mathbf{Z})\mathbf{U} + (\mathbf{R} + \mathbf{Z}\mathbf{C}\mathbf{Y})\mathbf{W} + \mathbf{Q}\mathbf{W} \\ \mathbf{O} &= (\mathbf{R}^+ + \mathbf{Y}\mathbf{C}\mathbf{Z})\mathbf{U} + (\mathbf{R} + \mathbf{G} + \mathbf{Y}\mathbf{C}\mathbf{Y})\mathbf{W} + \mathbf{Q}\mathbf{U} \\ \mathbf{O} &= \mathbf{Q}^+(\mathbf{U} + \mathbf{W}) + \mathbf{H}\mathbf{V}\end{aligned}\tag{1}$$

where \mathbf{C} and \mathbf{R} are the coulomb and repulsive interaction matrices. The breathing

matrices \mathbf{Q} , \mathbf{H} and \mathbf{V} are defined as

$$\mathbf{Q} = \begin{vmatrix} \mathbf{O} & \mathbf{G} \\ \mathbf{G} & \mathbf{O} \end{vmatrix}, \mathbf{H} = \begin{vmatrix} \mathbf{H}(11) & \mathbf{H}(12) \\ \mathbf{H}(21) & \mathbf{H}(22) \end{vmatrix}, \mathbf{V} = \begin{vmatrix} \mathbf{V}_1 \\ \mathbf{V}_2 \end{vmatrix} \quad (2)$$

where \mathbf{G} and \mathbf{H} are the dynamical matrices corresponding to “shell-breathing” and “breathing-breathing” force constants and \mathbf{V} is 2-vector breathing amplitude matrix, \mathbf{G} is a 3-vector breathing matrix, \mathbf{Q} is a (6×2) matrix. The explicit expressions for these force constants are reported elsewhere [26].

The method of determination of the parameters involved in the force constants matrices is quite straight forward. These parameters are related to the bulk properties such as elastic and dielectric constants. In table 1 we present the input constants and in table 2 the derived model parameters for Yb-pnictide compounds.

3. Results and discussion

In deriving the model parameters we have considered only five short-range force constants and four shell model parameters. Due to lack of sufficient macroscopic

Table 1. Input constants for ytterbium pnictides. Elastic constants are in 10^{12} dyn/cm², frequency in THz, r_o in Å, α_1 and α_2 in Å⁺³ [15, 16].

Properties	YbN	YbP	YbAs
r_o	2.3905	2.7688	2.8488
C_{11}	3.8500	2.7000	2.5000
C_{12}	1.0800	1.5000	1.4700
C_{44}	1.2900	0.6200	0.4700
ω_{TO}	8.2290	6.2800	5.3100
α_1	0.6000	0.6100	0.7300
α_2	-0.2343	0.7769	1.3689
$\epsilon_0/\epsilon_\infty$	12.6500	11.487	7.515

Table 2. Output parameters for Yb-pnictides. All are in units of $e^2/2V$, except Y which is in e and Z (dimension-less).

Parameters	YbN	YbP	YbAs
A_{12}	53.21782	68.18918	76.65823
B_{12}	-11.03196	-9.06572	-4.81384
A_{11}	-1.9070	0.04817	2.28000
B_{11}	1.9945	-2.27000	-6.41569
A_{22}	0.23844	-5.71000	-9.15237
$Y_1 = Y_2$	6.44	7.01	5.70692
G_1	2424.86	3276.89	2058.85
G_2	-4657.9243	2572.71	1097.899
Z	2.60	2.70	2.8

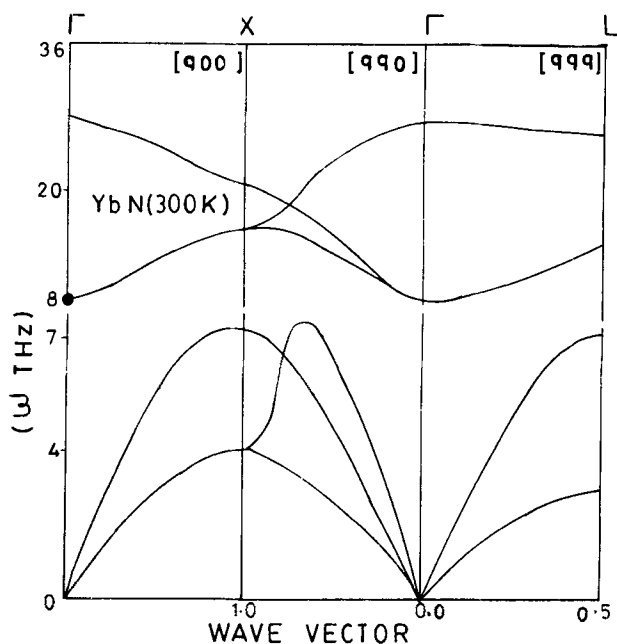


Figure 1. Phonon dispersion curves for YbN using BSM.

properties the shell charges for Yb and pnictide elements are considered to be equal. The calculated phonon dispersion curves (PDC) are plotted in figures 1–3.

In YbN, due to small mass of nitrogen atom, we obtain very large values of longitudinal optical (LO) frequencies. The acoustic branches however remain comparatively small in magnitude and show a smooth variation along all the directions of the Brillouin zone (BZ). Since the present model assumes the Yb-pnictides to behave like ionic crystals, as in Eu-chalcogenides [21, 22], we obtain a large splitting between LO and TO modes. This shows that the ionicity in this compound is large thereby indicating a strong Coulomb interactions. This behaviour is also observed in other two compounds of this series, a characteristic not observed in the PDC of TmSe, SmYS and some other rare earth intermediate valence compounds (REIVC) [12–14, 24]. This is mainly because of the fact that the later class of REIVC shows anomalous behaviour in their elastic constants. The ratio of elastic constants C_{11} to C_{12} in REIVC is much larger than that of the Yb-pnictides. In addition this large LO-TO splitting obtained from the present calculations of the PDC of Yb-pnictides could be understood from the electronic density of states and dielectric response measurement, which are, unfortunately not available at present.

A systematic trend of variation of LA phonon in all the three compounds is observed. As the polarizability of pnictide ion increases a hump near the X-point in Δ direction from YbN to YbAs of BZ gradually appears. This hump is maximum in YbAs. It is revealed from figures 1 to 3 that the crossover between TO and LA branches at L-point of the BZ increases from YbP to YbAs due to increase in mass and polarizability of the pnictide ions.

In figure 4, we have plotted two effective radial force constants calculated from the present model as a function of the lattice parameter. The dominance of the Yb-X force constant in all the Yb-pnictides has been observed. In addition, the small (or

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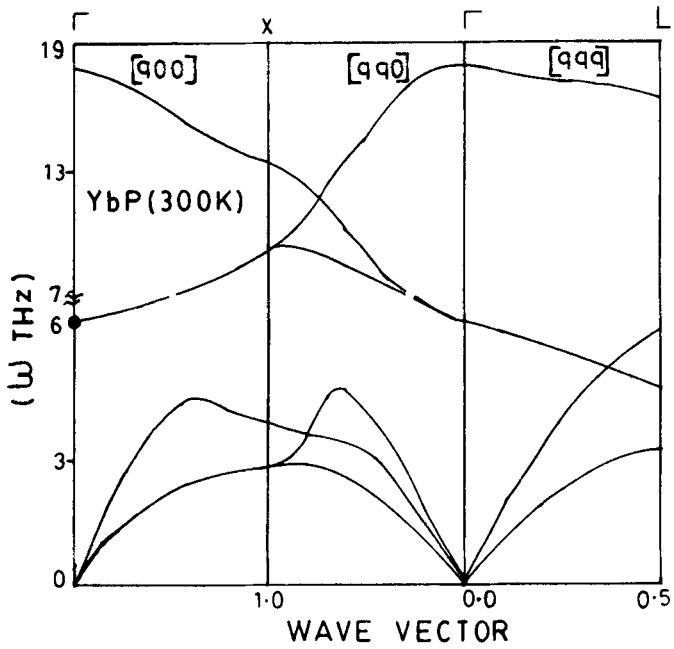


Figure 2. Same as in figure 1 for YbP.

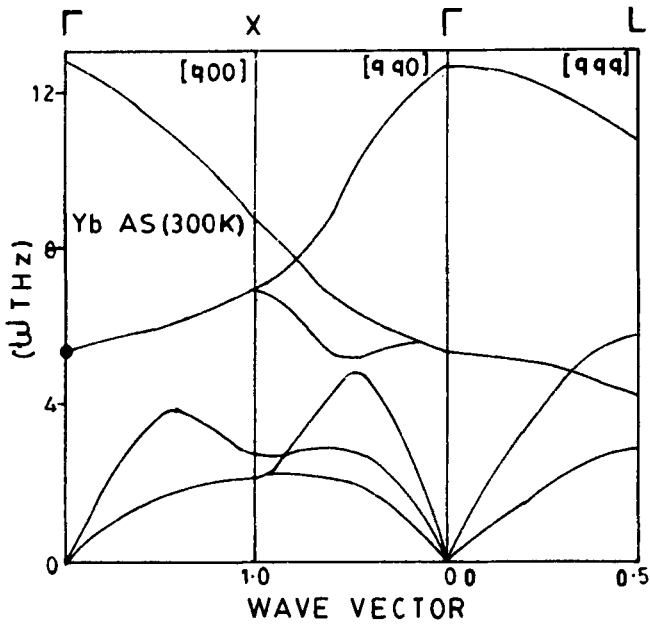


Figure 3. Same as in figure 1 for YbAs.

negative) magnitude of the Yb-Yb force constant shows that the large size of the second neighbour force constants are not significant due to large size of the pnictide ions. The small magnitudes of Yb-N or Yb-Yb force constants, as compared to those of

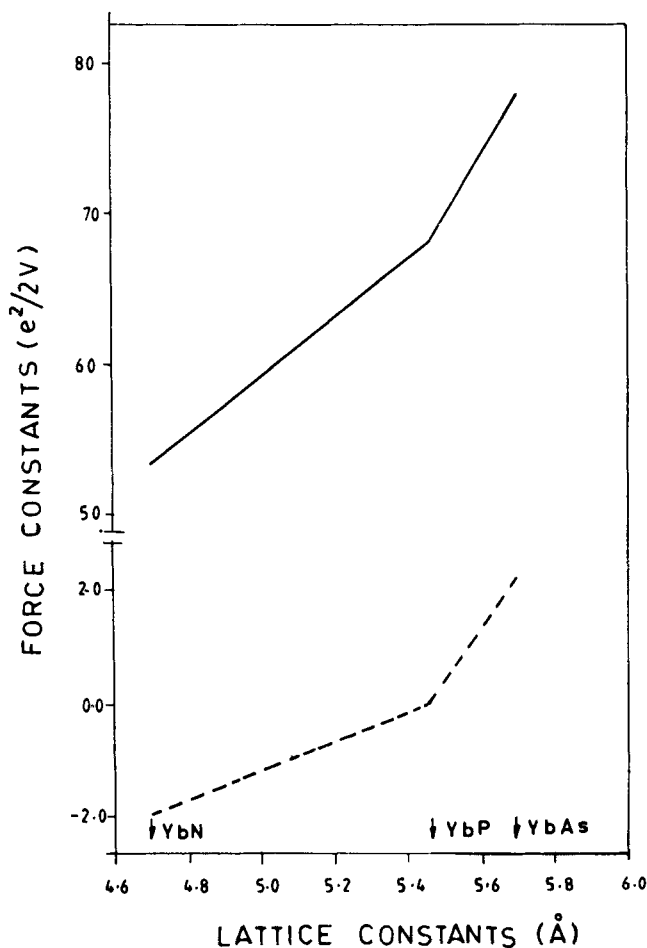


Figure 4. The Yb-X and Yb-Yb radial force constants as a function of lattice parameter. Solid and dashed curves are for Yb-X and Yb-Yb respectively.

other two members of this family reveal that the valence electrons might have some influence on the force constants of YbN.

The phonon density of states is an important dynamical property as its computation needs phonon frequencies in entire Brillouin zone. The one phonon density of states for three ytterbium pnictides have been obtained from BSM and are plotted in figures 5–7. In YbN, the density of states is very small (or nearly zero) in the range of 8 to 10 THz which is in accordance with the PDC. We observe the peaks distributed mainly around three frequency ranges. The distributed peaks between 2 and 7 THz are due to TA(X), LA(X), LA(L) and TA(L) modes. Two peaks with large intensity around 14 THz are also obtained which may be assigned to TO(L) and TO(X) phonons. The peaks between 20 and 26 THz are mainly contributed by the LO phonons at X and L points. The one phonon density of states for YbP and YbAs is plotted in figures 6 and 7 respectively which reveal more or less similar features as observed in YbN. The peaks observed at smaller frequency region are due to TA(X), LA(X) and TA(L), while those in the higher frequency region of the spectrum are due to optical phonons. Since no measurement of Raman and IR spectra has been reported so far, these peaks could not

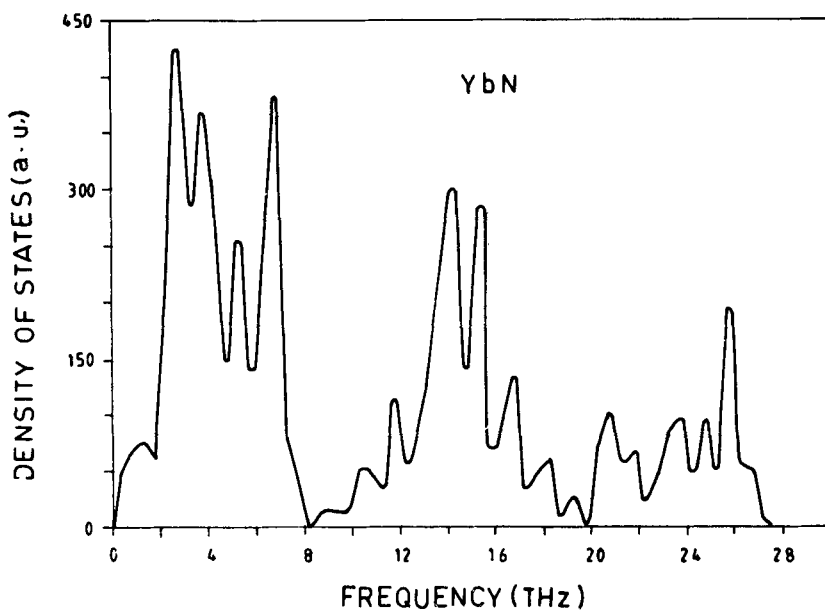


Figure 5. One phonon density of states for YbN.

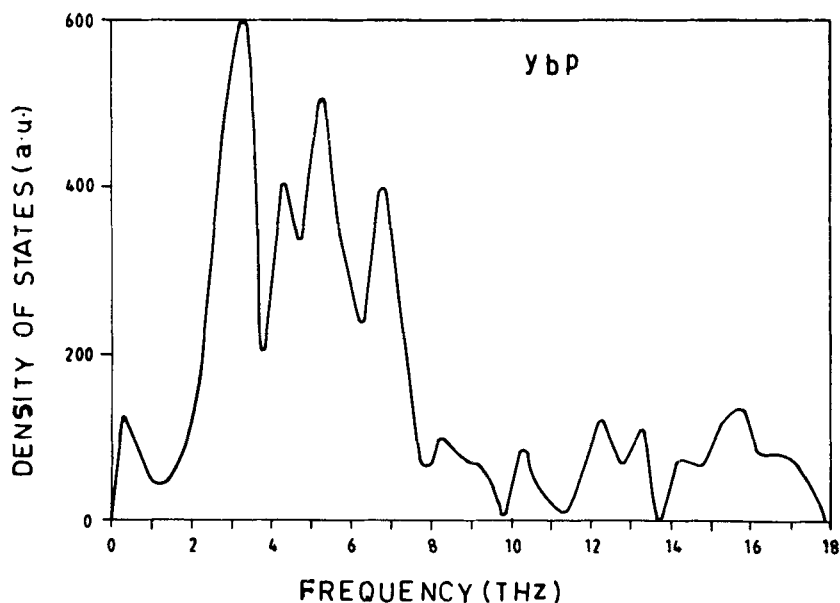


Figure 6. Same as in figure 5 for YbP.

be compared with experiment at present in detail. It is expected that these will be useful when such measurements are carried out.

Finally, we have reported for the first time the complete phonon dispersion curves and one phonon density of states for Yb-pnictides by using the breathing shell model

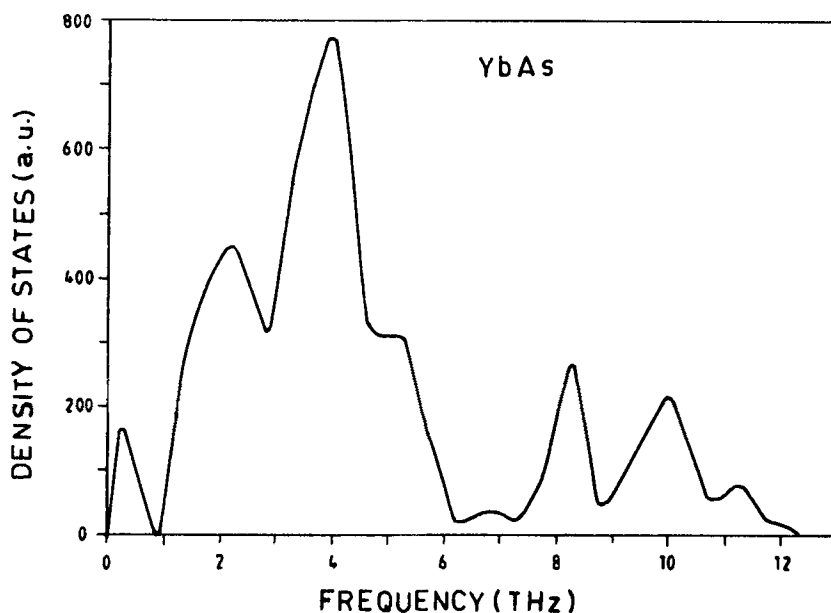


Figure 7. Same as in figure 5 for YbAs.

which incorporates the breathing motion of electron shell. Due to non-availability of sufficient experimental measurements, we could not compare our investigated results on PDC and phonon density of states with observed data. The PDC of Yb-pnictides reveal, in principle, the ionic nature of these rare earth pnictides similar to Eu-chalcogenides [21, 22]. We emphasize the necessity of further Raman and neutron scattering measurements in these compounds.

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