

## Lattice vibrations in Yb-pnictide compounds

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We have investigated the lattice vibrational properties of the rare-earth (RE) Yb-pnictide compounds by using a three-body force rigid-ion model suitable for these compounds. The calculated phonon-dispersion curves (PDC) reveal that these compounds do not show any anomaly in their phonon properties, particularly in view of their recently measured elastic and optical properties, such as shown by other RE compounds having NaCl structure. We emphasize the need of measurements of the complete PDC of Yb-pnictide compounds to support the recent results on elastic, optic, and the presently calculated phonon properties.

### I. INTRODUCTION

The rare-earth (RE) pnictides and chalcogenides have, in the recent past, drawn considerable interest of the solid-state and materials scientists because of their diverse electronic, magnetic,<sup>1-5</sup> optical, dielectric, and phonon<sup>6,7</sup> properties. The special characteristic of these materials is the fluctuation in valence. In several RE compounds, the rare-earth ion has the electronic configuration  $4f^{n-1}(5d6s)^m$ , where the  $4f$  band is partially filled. Under the influence of pressure or temperature, the valence of the RE ion changes to  $4f^{n-1}(5d6s)^{m+1}$ . Most of the RE pnictides and chalcogenides crystallize in the NaCl structure. 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,  $\text{TmS}_x\text{Se}$ .<sup>8-14</sup> 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.<sup>12-14</sup> Both semiconducting and metallic behavior 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.<sup>15,16</sup> These authors have measured the elastic constants using Brillouin scattering and a surface acoustic wave (SAW) technique<sup>15</sup> and optical and phonon properties using reflectivity measurements and Raman spectroscopy<sup>16</sup> for large single crystals of RE-pnictide compounds. They have established that these compounds are self-compensated semimetals with an indirect overlap of  $p$  and  $d$  bands. The metallic nature, however, arises because of nonstoichiometric nature of the crystals, a behavior more prominent in YbN, in comparison to YbAs and YbP. These authors<sup>15,16</sup> have also emphasized that this group of RE compounds are weakly intermediate valent (or moderate Kondo systems) with semimetallic 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<sup>15</sup> reveals that none of these materials show anomalies in their elastic properties, such as those observed in the case of  $\text{Sm}_x\text{Y}_{1-x}\text{S}$ ,<sup>14</sup> YS,<sup>17</sup> TmSe,<sup>13,14</sup> and some of the

uranium pnictides and chalcogenides.<sup>18-20</sup> 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.<sup>2,21</sup> On the contrary, the elastic properties are quite similar to those of RE europium chalcogenides ( $\text{EuX}$ ,  $X=\text{O}$ , S, Se, Te) which do not exhibit valency fluctuation.<sup>22,23</sup>

On the other hand, not much can be concluded about metallic and semimetallic nature from the Raman measurements<sup>16</sup> on the optical and phonon properties of these materials. However, complete measurements on the phonon dispersion curves by neutron-scattering experiments can lead to some significant results. Motivated by the recent measurement of elastic constants and zone-center optical frequency, we are impeded to calculate the complete phonon dispersion curves of these compounds with the help of the measured information provided in Refs. 15 and 16 by using suitable theoretical model in order to establish further the physical properties of this group of compounds. We briefly outline the theory in Sec. II and present our calculated results in Sec. III.

### II. THE THEORETICAL MODEL

In the absence of any measured data on the phonon dispersion curves, except the  $\omega_{\text{TO}}(\Gamma)$ , it is very difficult to choose a suitable model to predict them. In selecting the present lattice dynamical model (e.g., three-body force rigid-ion model), we find the following arguments in support of this choice: (i) The authors in Refs. 15 and 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 intermediate valence compounds,  $\text{Sm}_{0.75}\text{Y}_{0.25}\text{S}$  and TmSe.<sup>12-14</sup> (ii) The measured elastic constants<sup>15</sup> for Yb pnictides do not exhibit anomalous behavior, 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<sup>18,19</sup> is expected to be absent. (iii) It is a simpler model with a smaller number of parameters.

In view of the above discussions, we have chosen the

three-body rigid-ion model (TRIM) which has been found extremely successful in explaining the phonon properties of a wide class of rare-earth compounds<sup>13,22</sup> and uranium compounds.<sup>19</sup> The three-body force included in the present calculations arises from electronic charge transfer between the rare-earth ions and their nearest neighbors. Details of this type of interaction in ionic solids and semiconductors have been discussed by Singh<sup>24</sup> and briefly outlined below. The general formalism of TRIM can be derived from the crystal potential energy expressed as<sup>25</sup>

$$\begin{aligned}
 U(r) = & \frac{1}{2} \sum_{lk'l'k'} \sum_{(lk \neq l'k')} \frac{z_k z_{k'} e^2}{|r(lk; l'k')|} \\
 & + \frac{1}{2} \sum_{lk} \sum_{l'k'} \phi^R[|r(lk; l'k')|] \\
 & + \sum_{lk} \sum_{l'k'} \sum_{l''k''} z_k e f_k[r(lk; l''k'')] \frac{Z_{k'} e}{|r(lk; l'k')|}, \quad (1)
 \end{aligned}$$

where the first two terms represent the usual two-body long-range Coulomb and short-range repulsive interaction potentials. The last term contains interactions of three-body character<sup>25,26</sup> which can be calculated as if a charge  $\Delta q = \pm Z_k e f(r)$  is transferred to the ion  $(lk)$  from the neighboring ion  $(l''k'')$  due to the overlap of electron shells and this in turn interacts with  $Z_{k'} e$  at  $(l'k')$  via Coulomb's law. Here  $f(r)$  is a function proportional to the square of the overlap integrals<sup>25,26</sup> between two neighboring ions and dependent on the separation  $(r)$  between them.

Based on Eq. (1) and postulating the overlap repulsion effective up to the second neighbors and following closely the method of Woods, Cochran, and Brookhouse,<sup>27</sup> the equation of motion of TRIM can be written as

$$\omega^2 M U = (R + Z_m C' Z_m) U, \quad (2)$$

where  $Z_m e = Z[1 + 6f(r_0)]e$  denotes the effective ionic charge<sup>28</sup> modified from its original values  $Ze$ .<sup>24,27</sup> In view of the smallness of three-body force parameter  $f_0 [=f(r_0)]$ , we can write  $Z_m = Z(1 + 12f_0)^{1/2}$ , since  $(1 + 6f_0)^2$  can be approximated as  $(1 + 12f_0)$ .<sup>29</sup> The expressions required to evaluate  $R$  have already been derived by Cowley,<sup>30</sup>  $C'$  represents the modified long-range interaction matrix given by

$$C' = C + Z_m^{-2} Z r_0 f_0' V, \quad (3)$$

where  $C$  and  $V$  are the Coulomb and three-body interaction matrices already defined and evaluated by Kellerman<sup>31</sup> and Verma and Singh,<sup>32</sup> respectively.

The dynamical matrix corresponding to the present model is

$$D(q) = R + Z_m C' Z_m, \quad (4)$$

leading to secular determinant

$$|D(q) - M\omega^2| = 0. \quad (5)$$

The phonon eigenvalues are usually obtained by solving Eq. (5).

TABLE I. Input constants for ytterbium pnictides. Elastic constants are in  $10^{12}$  dyn/cm<sup>-2</sup>. Frequency in THz,  $r_0$  in Å (Refs. 15 and 16).

Properties	YbN	YbP	YbAs
$r_0$	2.3905	2.7680	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
$\omega_{T0}$	8.2290	6.2800	5.3100

The present model has four short-range parameters ( $A_{ij}$  and  $B_{ij}$ ,  $i, j = 1, 2$ ) and one TBI parameter  $Z_m$ . The quantities  $A_{ij}$  and  $B_{ij}$  are defined as follows:<sup>29</sup>

$$\begin{aligned}
 \frac{e^2}{2V} (A_{ij}) &= \left( \frac{d^2 \phi_{ij}^R(r)}{dr^2} \right)_{r=r_0}, \\
 \frac{e^2}{2V} (B_{ij}) &= - \left( \frac{1}{r} \frac{d \phi_{ij}^R(r)}{dr} \right)_{r=r_0}, \\
 \frac{e^2}{2V} (A_{ii}) &= \left( \frac{d^2 \phi_{ii}^R(r)}{dr^2} \right)_{r=r_0\sqrt{2}}, \\
 \frac{e^2}{2V} (B_{ii}) &= - \left( \frac{1}{r} \frac{d \phi_{ii}^R(r)}{dr} \right)_{r=r_0\sqrt{2}}, \quad (6)
 \end{aligned}$$

where  $V$  is the volume of unit cell.  $\phi_{ij}^R$  are short-range interaction potentials of Born-Mayer type.

All the parameters can be self-consistently determined by using the expressions for elastic constants, equilibrium condition, zone-center optical frequencies, the expression of which is given in the Appendix. In calculating the phonon spectrum of Yb pnictides, however, we have neglected Yb-Yb interactions because of their smaller ionic size, and less number of experimental data available for them. This model has already been used previously by us to interpret the phonon properties in U compounds<sup>19,20</sup> and other rare-earth compounds.<sup>13,23</sup> In Table I we present the input constants and Table II shows the derived model parameters for Yb-pnictide compounds.

### III. RESULTS AND DISCUSSIONS

In deriving the model parameters we have considered only four short-range force constants and one TBI parameter.

TABLE II. Output parameters for Yb pnictides.

Parameters	YbN	YbP	YbAs
$A_{12}$	29.6593	33.7293	39.7313
$B_{12}$	-2.0185	-5.0185	-6.0185
$A_{22}$	3.5091	3.0908	2.0988
$B_{22}$	-0.1621	-0.5621	-1.2621
$Z_m$	1.1512	1.1306	1.0701

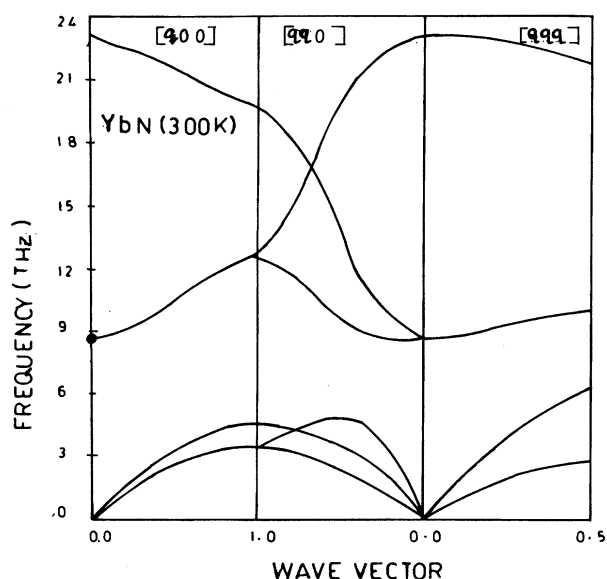


FIG. 1. Phonon dispersion curves for YbN using TRIM.

The calculated phonon dispersion curves (PDC's) are plotted in Figs. 1–3.

In the case of YbN, due to a small mass of nitrogen atoms, 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 behave like ionic crystals, as in the case of Eu chalcogenides,<sup>22,23</sup> we obtain a large splitting between LO and TO modes. This shows that the ionicity in this compound is large thereby indicating strong Coulomb interaction is responsible for crystal cohesion. This behavior is also observed in the other two com-

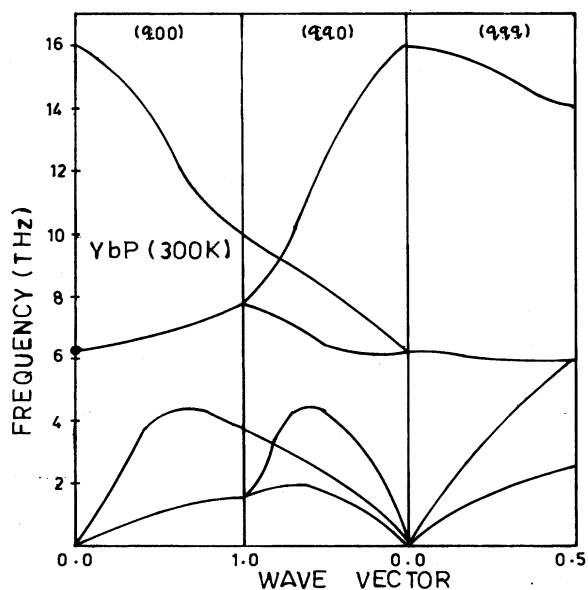


FIG. 2. Same as in Fig. 1 for YbP.

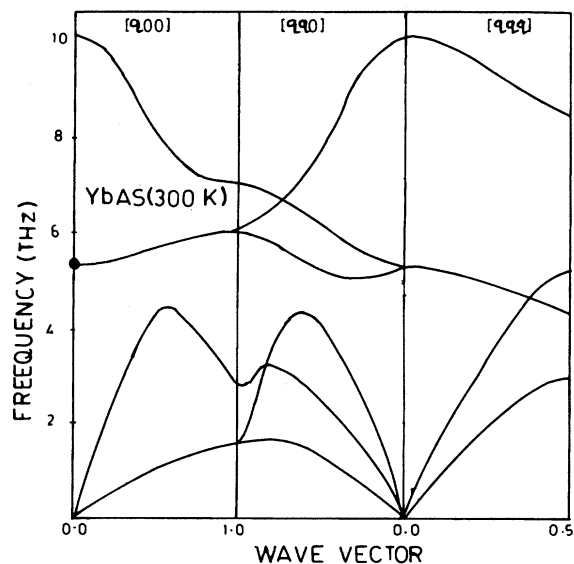


FIG. 3. Same as in Fig. 1 for YbAs.

pounds of this series, a characteristic not observed in the PDC's of TmSe, SmYS, and some other rare-earth intermediate valence compounds (REIVC).<sup>12–14</sup> This is mainly because of the fact that the later class of REIVC's show anomalous behavior 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 can be understood from the electronic density of states and dielectric response measurements, which are, unfortunately not available at present.

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

The phonon density of states is an important dynamical property as its computation needs phonon frequencies in the entire Brillouin zone. The one-phonon density of states for three ytterbium pnictides has been obtained from TRIM and is plotted in Figs. 4–6. In the case of YbN, the density of states is very small (or nearly zero) in the range 6.5–8.5 THz which is in accordance with the PDC. We observe that the peaks are distributed mainly around three frequency ranges. The two main peaks between 2 and 6 THz are due to TA(X), LA(X), LA(L), and TA(L) modes. Two peaks with large intensity between 9 and 12.5 THz are also obtained which may be assigned to TO(L) and TO(X) phonons. The peaks between 15 and 22.5 THz are mainly contributed by the LO phonons at X and L points. The one-phonon density of states for YbP and YbAs are plotted in Figs. 5 and 6, respectively, which reveal more or less similar features as observed in the case of YbN. The peaks observed at smaller frequency region

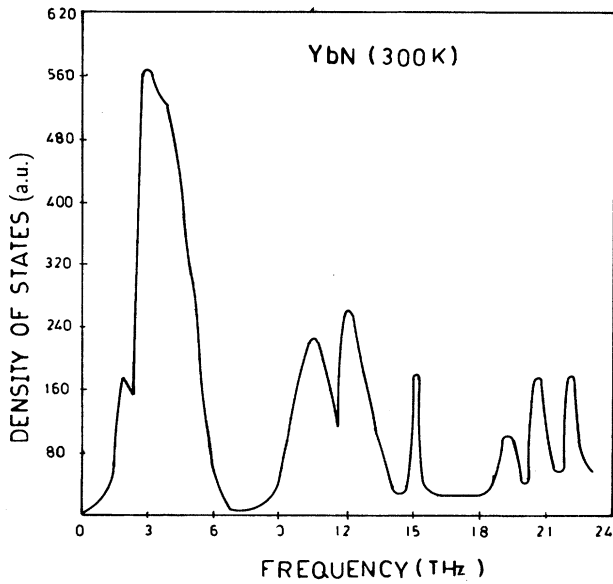


FIG. 4. One-phonon density of states for YbN.

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 detailed measurement of Raman and IR spectra has been reported so far, these peaks could not be compared with experiment at present. It is expected that these will be useful when such measurements are carried out. In our present paper we find our results are more or less in agreement with some of the predictions made in Refs. 15 and 16. First, the force constants presented in Table II vary systematically with increase in mass from YbN to YbAs. Second, in agreement with experiment<sup>33</sup> we observe a large peak in the one-phonon density of states at 16.52 meV due to acoustic mode, which was predicted to be between 15 and 20

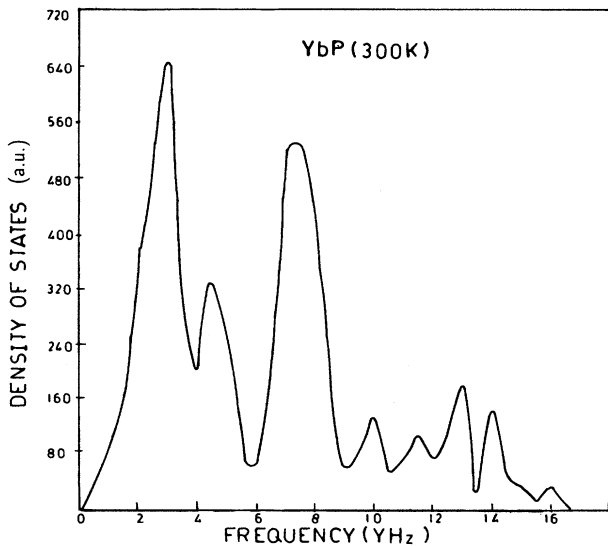


FIG. 5. Same as in Fig. 4 for YbP.

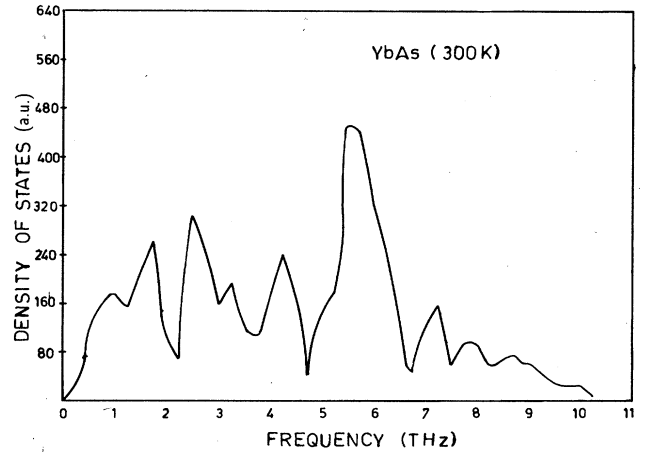


FIG. 6. Same as in Fig. 4 for YbAs.

meV for YbN. Since we use a simple model to calculate the dispersion curves of Yb pnictides by using experimental data from Refs. 15 and 16 any other comparison between our results and those reported in Refs. 15 and 16 will be unfair.

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 three-body force rigid-ion model which incorporates the charge-transfer effects between neighboring ions. Due to nonavailability 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.<sup>22,23</sup> We emphasize the necessity of further Raman and neutron-scattering measurements in these compounds.

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#### APPENDIX

The expressions for the elastic constants derived from the dynamical matrix of TRIM are given by<sup>29</sup>

$$C_{11} = (e^2/4r_0^4) [-5.112Z_m^2 + A_{12} + \frac{1}{2}(A_{11} + A_{22}) + \frac{1}{2}(B_{11} + B_{22}) + 9.3204Zr_0f'_0], \quad (A1)$$

$$C_{12} = (e^2/4r_0^4) [0.226Z_m^2 - B_{12} + \frac{1}{4}(A_{11} + A_{22}) - \frac{5}{4}(B_{11} + B_{22}) + 9.3204Zr_0f'_0], \quad (A2)$$

$$C_{44} = (e^2/4r_0^4) [2.556Z_m^2 + B_{12} + \frac{1}{4}(A_{11} + 3B_{11}) + \frac{1}{4}(A_{22} + 3B_{22})]. \quad (A3)$$

By using the derivations for the short-range force constants in Eq. (1) of the text and imposing it to the equilibrium condition

$$\left(\frac{dU(r)}{dr}\right)_{r=r_0} = 0,$$

we get

$$B_{11} + B_{22} + B_{12} = -1.165 Z_m^2, \quad (\text{A4})$$

Following usual procedure, the long-wave optical vibration frequencies ( $\omega_L, \omega_T$ ) can be written as<sup>29</sup>

$$\mu \omega_L^2 = R_0 + (8\pi/3V)[(Z_m e)^2](1 + 6Z_m^{-2} Z r_0 f'_0), \quad (\text{A5})$$

$$\mu \omega_T^2 = R_0 - (4\pi/3V)(Z_m e)^2, \quad (\text{A6})$$

where  $R_0 = (e^2/V)(A_{12} + 2B_{12})$ .

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