

Lattice mechanical properties of some fcc f-shell metals

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Abstract. A pseudopotential depending on an effective core radius is proposed to study the binding energy, equation of state, ion–ion interaction, phonon dispersion curves (\mathbf{q} -space and \mathbf{r} -space analysis), mode Grüneisen parameters and dynamical elastic constants of some fcc f-shell metals La, Yb, Ce and Th. The contribution of the s-like electrons is calculated in the second-order perturbation theory for the potential while d- and f-like electron is taken into account by introducing repulsive short-range Born–Mayer term. The parameter of the potential is evaluated by zero pressure condition. An excellent agreement between theoretical investigations and experimental findings is achieved which confirms the present formalism.

Keywords. Pseudopotential; binding energy; equation of states; phonon dispersion curves; elastic constants.

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1. Introduction

Various theoretical studies on simple, noble and transition metals [1–5] have been made so far based on pseudopotential theory but relatively few attempts have been made on rare-earth and actinide elements such as La, Yb, Ce and Th [6–17] by the same method. Phonon spectrum is the lattice characteristics which reflects the peculiarities of the interatomic interaction in a crystal. Rosengren *et al* [12] for the first time investigated the lattice dynamics of thorium using pseudopotential due to Krasko and Gurskii [13]. Jitendrakumar [14] proposed a two-parameter potential for the calculation of phonon dispersion relation for the thorium. Vrati *et al* [15] proposed single parametric pseudopotential for the same purpose. Singh and Singh [11] have calculated the phonon dispersion of La, Yb, Ce and Th. They used free electron part of pair potential, which is obtained in second-order perturbation theory using a rational dielectric function and Heine–Abarankov model potential [11]. They have considered valency $Z = 1.5, 2.0, 2.5$ and 3.0 . The potential parameters were chosen to give the exact value of phonon frequencies at zone boundary. Verma and Rathore [8] have calculated the phonon frequencies of thorium using the extended generalized exponential potential (EGEP), which contains three parameters. Hence, it involves more constraints in the study. Recently Pandya *et al* [16] have investigated the effects of overlaps and local field correction using the potential of Rosengren *et al* [12]. Later

on they have also [17] reported the phonon dispersion curves, phonon density of states, Debye–Waller factor, mean square displacements and equation of state for thorium. In order to interpret the results of complex structure of transition, rare-earth, actinides and noble metals it is highly desirable to have simple method of general applicability which can reproduce the results of most of the physical properties very close to the experimental findings. In all the above-mentioned studies no author has adopted a standard method to calculate the potential parameter. Hence in the present paper we thought it worthwhile to follow a unique method for the determination of potential parameter, which is free from any experimental fitting procedure.

2. Model potential

In every pseudopotential formalism either local or nonlocal approach has been used for the calculation of metallic properties [1–5]. As nonlocal pseudopotential is complicated to tackle, most of the people preferred to work on local pseudopotential. In the present article we have proposed a local form of pseudopotential, which includes in a simple parametric way all the features dictated by the physics of the situation. Particularly it is seen that in noble, transition and actinide metals, below the Fermi energy level there are filled d- and f-bands which tend to push up the energy of a given state. Hence, effect called ‘hybridization’ would require a repulsive term in the model potential. Hence, in \mathbf{r} -space, inside the core radius the model potential is a combination of repulsive and attractive terms (i.e. varying cancellation within the core). Beyond the core radius, the model potential is Coulombic in nature. In real space the potential is of the form (in Ryd.),

$$W(r) = -\frac{2Z}{r_c^2} \left[2 - \exp\left(1 - \frac{r}{r_c}\right) \right] r, \quad r < r_c$$

$$W(r) = -\frac{2Z}{r}, \quad r \geq r_c. \quad (1)$$

The bare ion form factor in the wave number space (\mathbf{q} -space) is of the form (in Ryd.),

$$W_B(q) = -\frac{8\pi Z}{\Omega_0 q^2} \left\{ \begin{aligned} &\frac{4(\cos qr_c - 1)}{q^2 r_c^2} + \frac{4 \sin qr_c}{qr_c} + \frac{\sin qr_c}{(1+q^2 r_c^2)^3} [5qr_c - 4q^3 r_c^3 - q^5 r_c^5] \\ &+ \frac{\cos qr_c}{(1+q^2 r_c^2)^3} [11q^2 r_c^2 + 4q^4 r_c^4 + q^6 r_c^6] + \frac{2eq^2 r_c^2 (q^2 r_c^2 - 3)}{(1+q^2 r_c^2)^3} - \cos qr_c \end{aligned} \right\} \quad (2)$$

where Z is the valency, Ω_0 the volume per ion, \mathbf{q} the wave vector and e the base of natural logarithm. It is evident that the potential contains only one parameter r_c and it has also the characteristics of exhibiting varying cancellation within the core. In addition the potential is continuous at $r = r_c$ and becomes weaker in the limit within the core $r \rightarrow 0$.

In the pseudopotential formalism it is necessary that the potential parameter can be determined properly. In the present work we have calculated the potential parameter from the zero pressure condition. The advantage of this method is that the potential does not bear any constraint due to a fitting procedure. Hence such a potential could be visualized as a parameter independent potential in the sense that the parameter is not determined by fitting it with any experimentally observed physical property of the system.

To consider the s–d–f hybridization and repulsion between the ions, we have introduced a Born–Mayer term $\alpha \exp(-r\beta)$ in the total energy calculations. The inclusion of such a

term was already justified by Onwuagba [18] and Antonov *et al* [19] for considering the effect of f-electron in the rare-earth metals and d-electrons in the transition metals. In the present calculation we have chosen the valence $Z = 2.0$ for all the metals and the other parameters used in the present calculations are given in table 1. We strongly emphasize the fact that we have not made fitting to experimental frequency at any symmetry points in the Brillouin zone. The Hartree dielectric function as modified by Taylor [20] has been used to obtain the screened form factor. We then used this particular combination of r_c and screening function to calculate the binding energy, equation of state, ion-ion interaction, phonon dispersion curves (\mathbf{q} -space and \mathbf{r} -space analysis), mode Grüneisen parameters and dynamical elastic constants of some fcc f-shell metals La, Yb, Ce and Th.

3. Binding energy and equation of states

The calculated values of binding energy of all four metals considered here are given in table 1 along with experimental and other such theoretical findings. Our presently calculated values of binding energy are in excellent agreement with the experiment and superior to the previously reported values [11,21].

The pressure-volume (P - V) relation is shown in figure 1 for La, Yb, Ce and Th. It may be noted that so far no one has reported theoretical P - V relation of these metals by pseudopotential except Pandya *et al* [17] and that too for thorium only. Our present P - V relation for La and Th are very close to the experimental findings. As there is no

Table 1. Input parameters and binding energies (in Ryd./ele.)

Metal	r_c (a.u.)	α	β	Binding energies (in Ryd./ele.)				
				Present	Expt. [11]	Others [11]	Others [11]	Others [21]
La	2.64922	125.9	2.151	1.5326	1.5519	1.5525	1.5507	1.4095
Yb	2.49615	258.8	1.80	1.5750	1.472	1.6944	1.6901	2.3661
Ce	2.48823	335.0	1.271	1.5681	1.5176	1.6346	1.6285	0.9191
Th	2.36221	182.16	1.150	1.5944	-	-	-	3.05

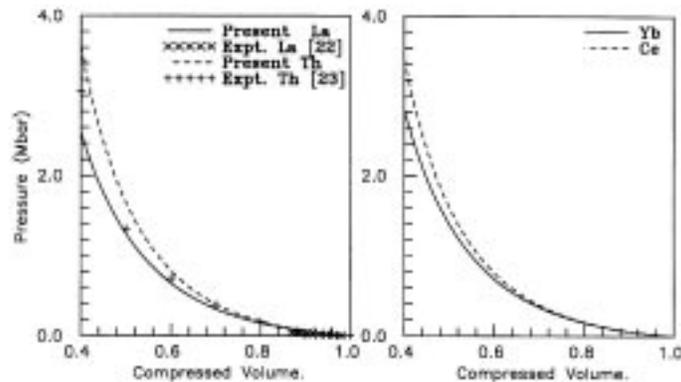


Figure 1. Pressure-volume relation for La, Yb, Ce and Th.

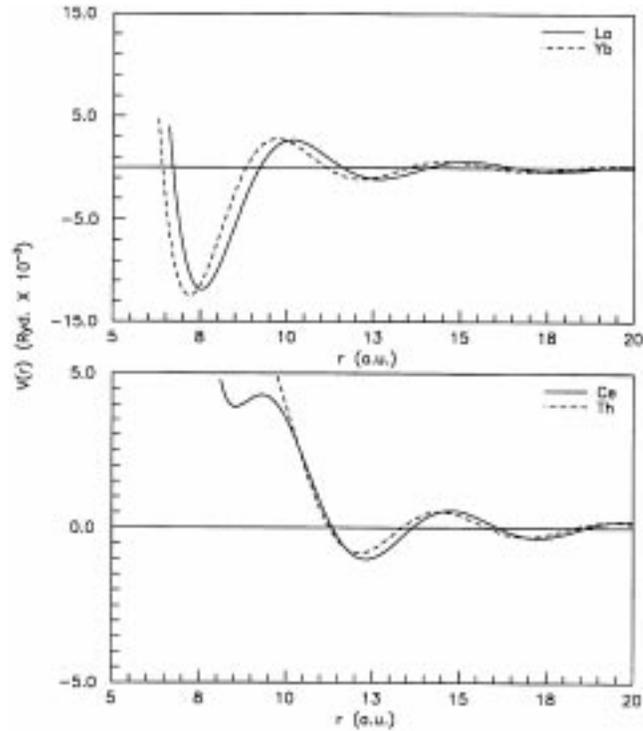


Figure 2. Ion–ion interaction for La, Yb, Ce and Th.

experimental data available for Yb and Ce, it is predictive in nature. Our P – V relation for thorium is much better than Pandya *et al* [17]. The better agreement of equation of states up to about 40% compression shows that the present model can be safely used for calculating lattice mechanical properties of compressed rare-earth and actinide elements.

4. Ion–ion interaction

In figure 2 we have displayed potential energy for La, Yb, Ce and Th. These potentials may be useful in lattice defect calculations since they show hard sphere-like behavior at small atomic separation.

5. Phonon dispersion curves (q-space and r-space analysis)

The dynamical matrix from which phonon energies and polarization vectors are calculated may be obtained either by summing real-space force constants or by performing a sum in reciprocal space. It is known that the real space sum converges faster than the more common reciprocal space sum and is more justifiable for the calculation of thermal properties and integral properties of the electron–phonon interactions. We have used both the methods, i.e., reciprocal space sum method as well as real space sum method for calculating the phonon dispersion relation of La, Yb, Ce and Th using our model potential.

Computations of the phonon frequencies along the three principal symmetry directions of the reciprocal lattice namely the $(0, 0, \xi)$, $(0, \xi, \xi)$ and (ξ, ξ, ξ) directions have been carried out. In addition, we have also included the $(1, \xi, 0)$ and $(1 - \xi, \xi, \xi)$ directions in the present investigations. The secular determinant in \mathbf{q} -space has been solved for 50 nearest neighbors [24] while in \mathbf{r} -space it has been solved for 32 nearest neighbors [25,26].

The phonon dispersion curves of La, Yb, Ce and Th are displayed for \mathbf{q} - and \mathbf{r} -space in figures 3–6 respectively. Our present phonon dispersion curves show significant improvement to that of the previously reported work. This fact must be regarded as the remarkable achievement of the present model. Onwuagba [18] and Wang and Overhauser [27] have calculated the phonon dispersion curves of La and Yb and having maximum deviation of 30% between theoretically calculated and experimental values. The results of Singh and Singh [11] have the maximum discrepancy of 20% at $[111]$ T mode for Ce, whereas for $[111]$ L mode of La, Yb, Ce and Th is found to be 5%, 30%, 17% and 26% respectively. The theoretical phonon dispersion curves obtained presently show better agreement with experiments than that achieved by others [11,18,27].

6. Phonon density of states (PDOS)

The phonon density of states, i.e., frequency distribution curves were obtained by using the root sampling technique in which 1685 q values were used to calculate the frequencies in $(1/48)$ th part of Brillouin zone. The number of frequencies so generated was 192×10^3 . Our results of DOS show good agreement with experimental findings and are shown in figure 7.

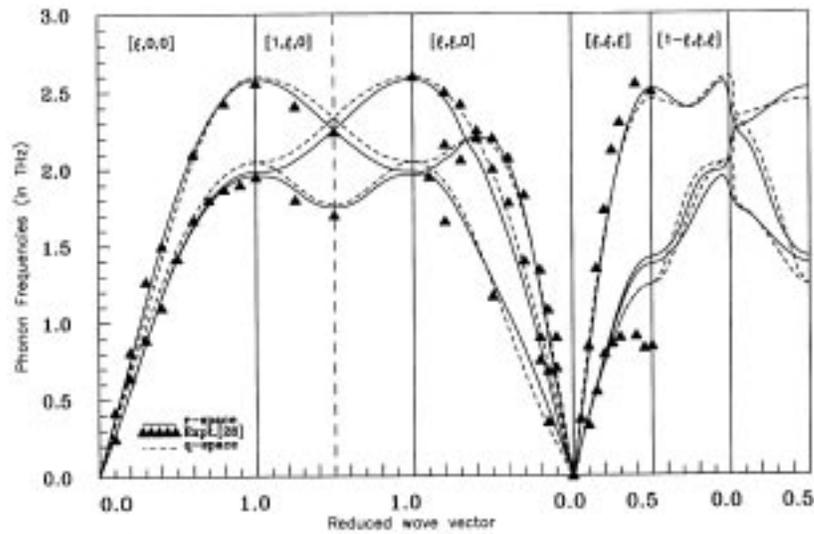


Figure 3. Phonon dispersion curves for La.

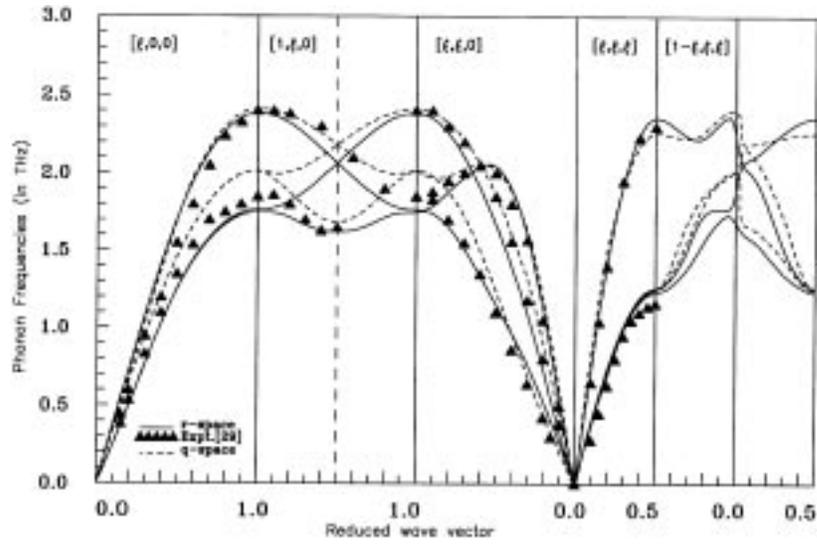


Figure 4. Phonon dispersion curves for Yb.

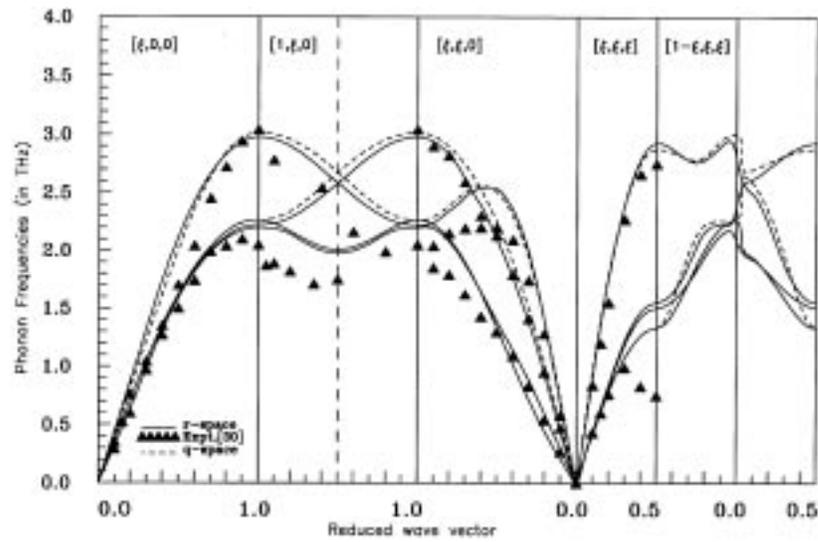


Figure 5. Phonon dispersion curves for Ce.

7. Debye temperature

The temperature dependence of lattice specific heat C_V is very useful for studying the theoretical phonon density of states. However, it is convenient to represent temperature dependence of Debye temperature. The Debye temperature θ_D at different temperatures

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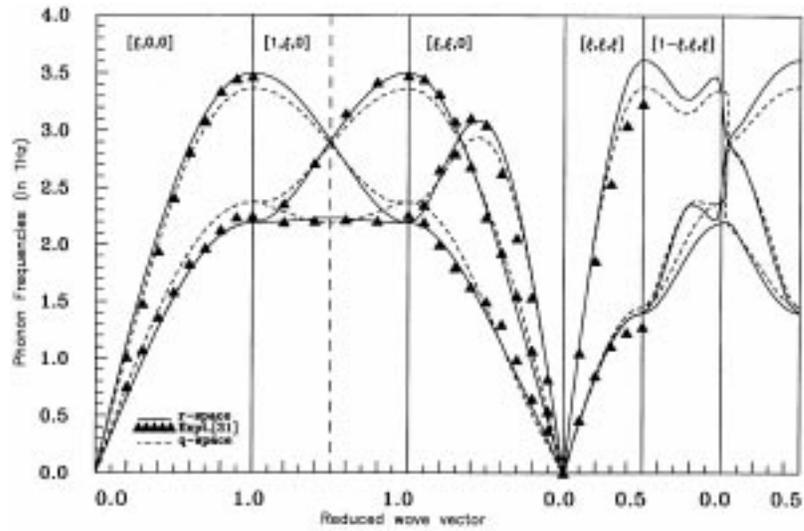


Figure 6. Phonon dispersion curves for Th.

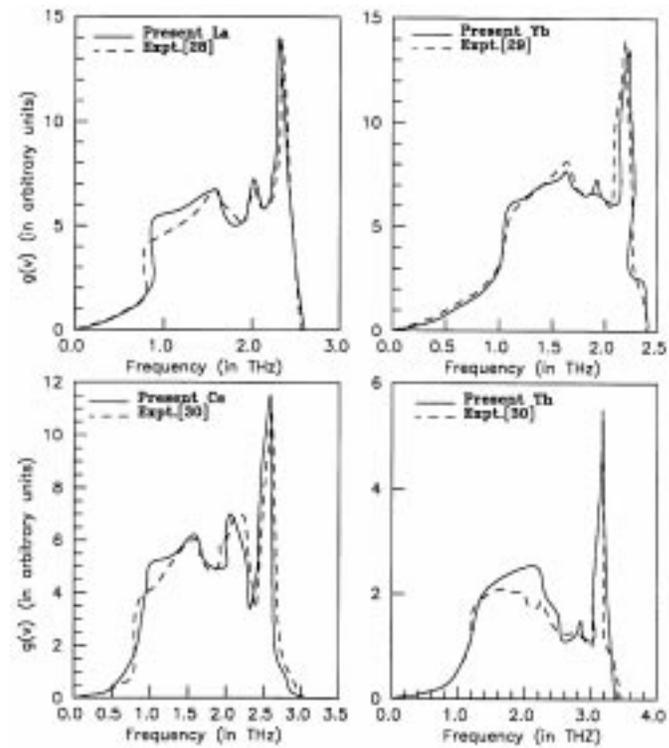


Figure 7. Density of states for La, Yb, Ce and Th.

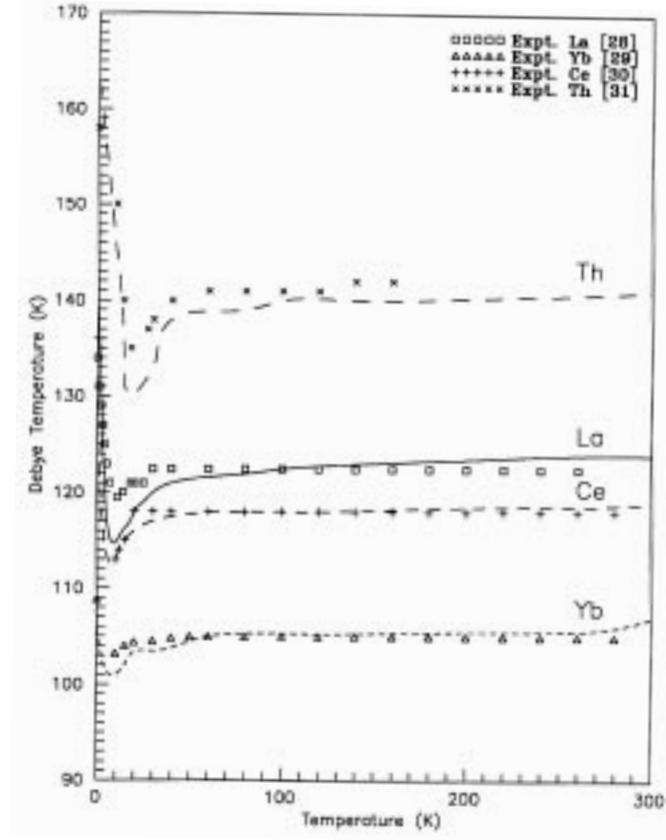


Figure 8. Debye temperatures for La, Yb, Ce and Th.

can be found by using standard tables $C_v/3R$ vs. θ_D/T [32]. In this case the deviation of $\theta_D(T)$ from constant indicates the difference between the observed heat capacity and that obtained in the Debye model. The results obtained are given in figure 8.

8. Mode Grüneisen parameters

The mode Grüneisen parameter $\gamma(\mathbf{q}, j)$ describes the change in the frequency $\omega(\mathbf{q}, j)$ of the phonon of wave vector \mathbf{q} and the branch index j with volume Ω and is defined by

$$\gamma(\mathbf{q}, j) = -\frac{d[\ln \omega(\mathbf{q}, j)]}{d[\ln \Omega]} \quad (3)$$

Figures 9–12 display the mode Grüneisen parameters as calculated presently in the high symmetry directions. To the best of our knowledge, the mode Grüneisen parameters of La, Yb, Ce and Th have not been measured. The experimental data, based on tunneling spectroscopy, indicates that the Grüneisen parameter is necessarily mode dependent and that the transverse modes are more sensitive to compression than the longitudinal one.

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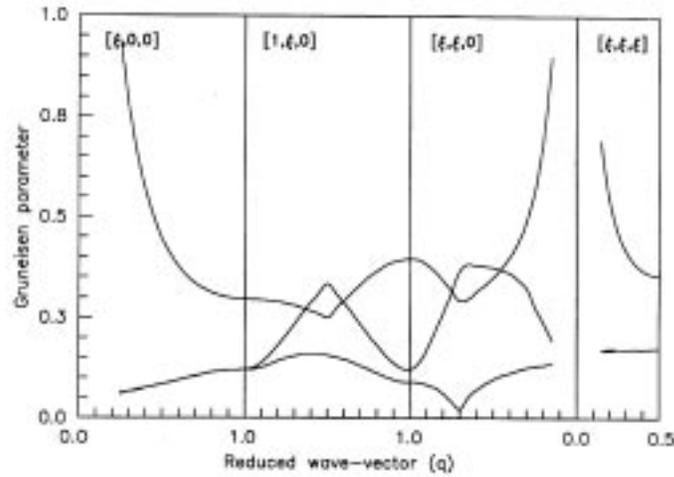


Figure 9. Mode Grüneisen parameters for La.

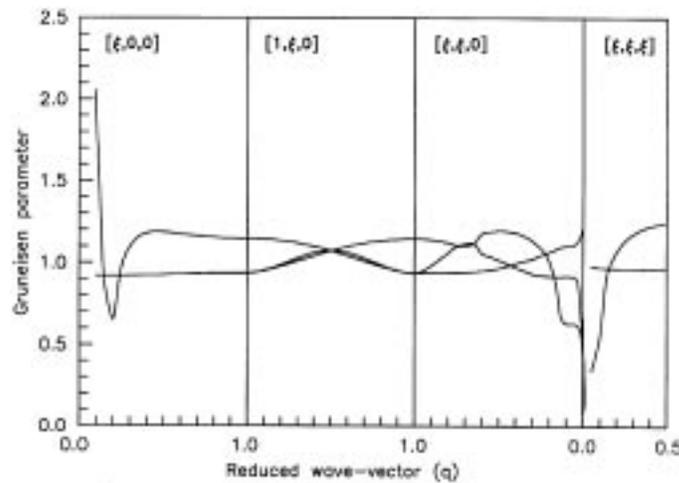


Figure 10. Mode Grüneisen parameters for Yb.

9. Dynamical elastic constants

The calculated values of C_{11} , C_{12} , C_{44} and bulk modulus are given in table 2 for La, Yb, Ce and Th respectively. These quantities are compared with the experimental and other such theoretical findings. In almost all the cases presently obtained theoretical values of elastic constants are better than or as good as those obtained by Singh and Singh [11] and Singh and Yadav [21] even though they have fitted their parameters with the experimental values. In the present work, we have not used any elastic constant for the determination of the

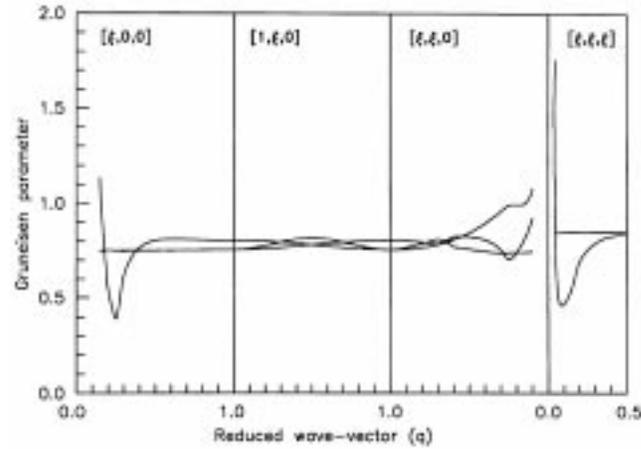


Figure 11. Mode Grüneisen parameters for Ce.

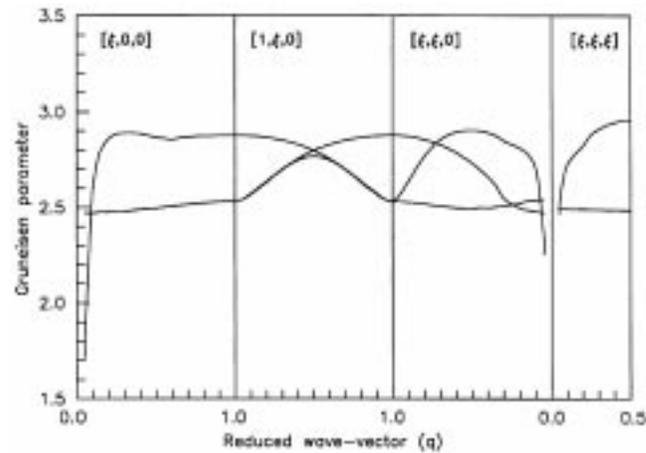


Figure 12. Mode Grüneisen parameters for Th.

Table 2. Elastic constants and bulk modulus (in 10^{12} dyne/cm²) of La, Yb, Ce and Th.

	La		Yb		Ce		Th	
	Present	Expt. [11]						
C_{11}	0.308	0.285	0.187	0.186	0.238	0.241	0.783	0.753
C_{12}	0.171	0.204	0.106	0.104	0.104	0.102	0.622	0.489
C_{44}	0.132	0.165	0.188	0.177	0.152	0.194	0.399	0.478
B	0.216	0.231	0.133	0.131	0.148	0.148	0.675	0.577

parameter. It is in this regard that the present model must be regarded as a meaningful improvement in the model due to Singh and Singh [11], Singh and Yadav [21] and Pandya *et al* [17].

In order to interpret the results of complex structure of transition metals, rare earth metals, actinides and noble metals it is desirable to have simple method of general applicability, which can reproduce the results of most of the physical properties very close to the experimental findings. The results so obtained are also comparable to those obtained from the most sophisticated methods, which are intricate and require lengthy calculations with large computer time. The approach we suggest is simpler and less time consuming. Thus, the method can readily be used for the relative ease and accuracy.

The present study of phonon dispersion curves leads to the following conclusions.

Our present results of phonon dispersion curves show significant improvement from the earlier works [11,16–18,27]. Still, whatever discrepancies are there can be rectified by the following way.

1. One should either use the non-local electron–ion interaction with suitable exchange and correlation interaction for d-electron or the ultrasoft pseudopotential with the local density approximation.
2. In all the calculations described above, the inner d-shell is assumed to be bound and static. In a realistic formalism the movement of bound d-shell around the nuclei should be incorporated.
3. To reproduce all the phonon anomalies, the exact electronic band structure should be included in the calculation of phonon frequencies of d-band metals.

The phonon dispersion curves are calculated for \mathbf{q} vectors lying in the major symmetry directions. On the other hand, for the density of state calculations one requires the calculations of frequencies for a large number of \mathbf{q} vectors distributed throughout the Brillouin zone. It is possible that for all the vectors the results may not be equally good. This is reflected in the density of state. Such results have been reported in literature in the past in the case of Cu [33–35]. In light of the fact that exhaustive study of lattice mechanical properties requires a large number of points in the Brillouin zone, it is difficult to perform by first principle methods and hence the appropriate pseudopotential calculations can still be useful.

Further, the earlier applications of model potentials were limited to fitting with experimental phonon frequencies at some symmetry points in the Brillouin zone. In light of the above facts, the successful application of the present study confirms the superior formalism of the pseudopotential developed in the present work.

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