LATTICE DYNAMICS OF ALUMINIUM, LEAD AND THORIUM ON MODIFIED BHATIA'S MODEL*

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Phonon dispersion relations along the three principal symmetry directions as well as lattice heat capacities of aluminium, lead and thorium have been calculated on the basis of the modified Bhatia model. The calculated results agree reasonably well with the experimental observations.

1. Introduction

Bhatia [1] has developed a phenomenological model for cubic metals about two decades ago. The mathematical simplicity and the physical rigor of this model have been responsible for the continued and present interest of workers in lattice dynamics. It has been used to compute the thermal properties of several cubic metals (see for example Gupta [2], Sanghal and Sharma [3] and references therein). Quite recently, his scheme has also been extended to h. c. p. metals. It was discovered by Shukla and Camargo [4] that Bhatia's expression for the electron-ion interaction matrix is erroneous and all workers using his scheme have invariably repeated it. Fullfilling the aforesaid correction in the electron-ion interaction matrix, Shukla and Salzberg [5, 6] have found that another modification, the consideration of ion-ion interaction beyond the first nearest neighbour, in Bhatia's model was found necessary in order to reproduce the experimental phonon dispersion relations in copper and sodium. Lately, the present authors have also applied such a scheme to study the lattice dynamics of all noble metals (Bertolo and Shukla [7, 8]). We could also obtain similar results for noble metals and f. c. c. transition metals as Shukla and Salzberg [5, 6] obtained for sodium and copper.

The great success of the modified Bhatia model for the aforesaid metals has encouraged us to take up the study of aluminium, lead and thorium on its basis. The reasons for considering these metals together were:

1. All of them are non-monovalent metals. Aluminium is trivalent and lead is tetravalent. In the absent of definie information about the valence of thorium, it was considered a divalent metal.

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2. While for lead and aluminium the experimental measurements of phonon frequencies have been available for a long time, for thorium such measurements have been performed only last year.

3. For all these metals extensive thermal and elastic data exist and this facilitates their lattice dynamical studies.

The lattice dynamics and heat capacities of lead, aluminium and thorium form the subject matter of this paper.

2. *Theory*

The secular determinant to determine phonon frequency is given by

$$|D - m\omega^2 \mathrm{I}| = 0, \tag{1}$$

where D is the dynamical matrix; m is the ionic mass; ω is the angular frequency; I is the unit matrix.

Each of the dynamical matrix is split up into two parts, the ion-ion interaction part D_{ij}^{ii} and the electron-ion interaction part, D_{ij}^{ie}.

$$D_{ij} = D_{ij}^{ie} + D_{ij}^{ii}. \tag{2}$$

Taking the ion-ion interactions up to the third neighbours, a typical diagonal and non diagonal part of the dynamical matrix is given by:

$$D_{ii}^{ii} = 2(2\alpha_1 + \beta_1)[2 - C_i(C_j - C_k)] + 4\alpha_1(1 - C_jC_k) + 4(\alpha_2 + \beta_2)[(1 - C_j^2) + 4\alpha_2 2 - (C_j^2 + C_k^2)]$$

$$+ \tfrac{8}{3}(2\beta_3 + 3\alpha_3)[1 + C_jC_k(1 - 2C_i^2)] + \tfrac{8}{3}(\beta_3 + 6\alpha_3)\left[1 + \frac{C_i}{2}(C_j + C_k)(1 - 2C_jC_k)\right], \tag{8}$$

$$D_{ij}^{ii} = 2\beta_1 S_i S_j + (\tfrac{4}{3}) S_i S_j \beta_3 [4C_k(C_i + C_j)(1 - 2C_k)^2]. \tag{4}$$

The electron-ion interaction has been taken on the basis of the work of Shukla and Camargo [4] and is given by:

$$D_{ii}^{ie} = \frac{K_e q_i^2 n^{-1}}{1 + q^2/k_c^2}, \tag{5}$$

$$D_{ij}^{ie} = \frac{K_e q_i q_d n^{-1}}{1 + q^2/k_c^2}, \tag{6}$$

where $S_i = \sin(q_i a)$, $C_j = \cos(q_j a)$, a — lattice parameter, q_i — i-th component of a phonon wave vector, $K_c = (r_s/a_0) K_F \beta$, r_s — radius of the atomic sphere, a_0 — Bohr radius, K_F — Fermi wave vector, (α_i, β_i) are force constants of i-th neighbour

$$.353 \leqslant \beta \leqslant .814, \quad n = 4/a^3.$$

By expanding the secular determinant in the long wavelength limit ($q \to 0$), the following relations were found between the elastic constants and force constants:

$$aC_{11} = 4\alpha_1+2\beta_1+4\alpha_2+4\beta_2+24\alpha_3+12\beta_3+aK_e, \tag{7}$$

$$aC_{12} = 4\alpha_1+\beta_1-4\alpha_2-24\beta_3+6\alpha_3+aK_e \tag{8}$$

$$aC_{44} = 4\alpha_1+\beta_1+4\alpha_2+24\alpha_3+6\beta_3, \tag{9}$$

where K_e is bulk modulus of the electron gas and is given by

$$K_e = (C_{12}-C_{44})+\frac{8}{a}(\alpha_1+\alpha_2+6\alpha_3). \tag{10}$$

3. *Numerical computations*

In order to determine the phonon frequencies it was necessary to evaluate the force constants. The seven disposable parameters of the model were evaluated by using the equations relating them to the three elastic constants and four experimental phonon frequencies corresponding to four wave vectors at the zone boundaries. After making several choices the final values of the frequencies selected for different metals are given in Table I.

TABLE I

Input data to calculate atomic force constants

Metal	Aluminium	Lead	Thorium
Elastic constants 10^{11}.dyn cm^{-1}			
C_{11}	11.373	5.437	7.530
C_{12}	6.191	4.505	4.890
C_{44}	3.128	1.819	4.780
Atomic mass 10^{-23} gm	4.48	39.94	3.853
Lattice parameter 10^{-8} cm	4.0251	4.924	5.0843
Phonon frequencies (THz)			
ν L 100	9.68		2.259
ν L.7.7.0	7.98	2.01	
ν L.5.5.5	9.64	2.15	3.24
ν L.900		2.05	
ν T 100		.89	
ν T.5.5.5	4.08		1.28
ν T.75.750	4.08		1.883

Care was taken to employ the elastic constants at the same temperature at which the experimental phonon frequencies were determined. The experimental phonon frequencies of aluminium were determined by Stedman and Nelsson [9] at 80°K. The phonon frequencies of lead were determined by Brockhouse et al. [10] at 100°K. The phonon frequencies to thorium were determined by Reese et al. [11] at the room temperature. The experimental values of the elastic constants of aluminium, lead and thorium were taken respectively from the measurements of Kamn and Alers [12], Waldorf and Alers [13] and that of Armstrong et al. [14]. The input data to calculate atomic force constants are given in Table I. The output values of the force constants are given in Table II.

TABLE II

Output values of the atomic force constants unit 10^3 dyn cm^{-1}

Metal	Aluminium	Lead	Thorium
α_1	−1.750	2.700	−4.350
β_1	25.036	−.488	30.210
α_2	−2.350	.777	−.400
β_2	5.091	−5.340	1.263
α_3	.004	.127	.107
β_3	.048	−1.258	1.672
ak_e	−18.422	47.215	−31.310

A knowledge of the numerical values of the force constants made it possible to calculate the phonon dispersion relations in aluminium, lead and thorium. Computed phonon dispersion curves of aluminium, lead and thorium are presented in Figs 1 to 3 together with the experimental points shown for comparison purposes. While the theoretical curve

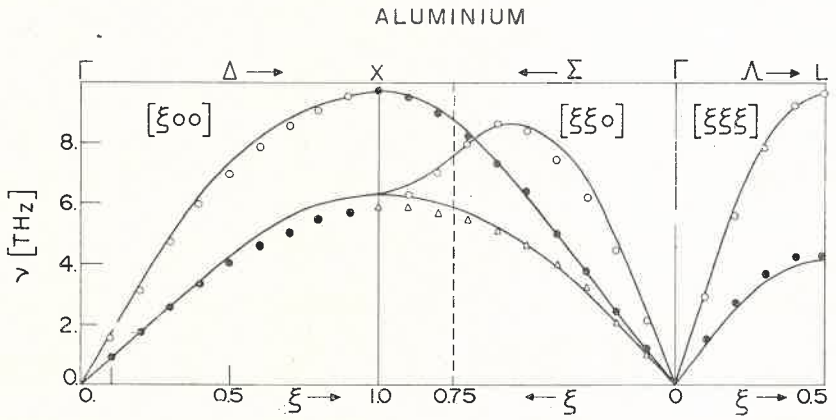

Fig. 1. Phonon dispersion relations in aluminium. Calculated curves are shown by a solid line. Experimental points are shown by ○, and Δ

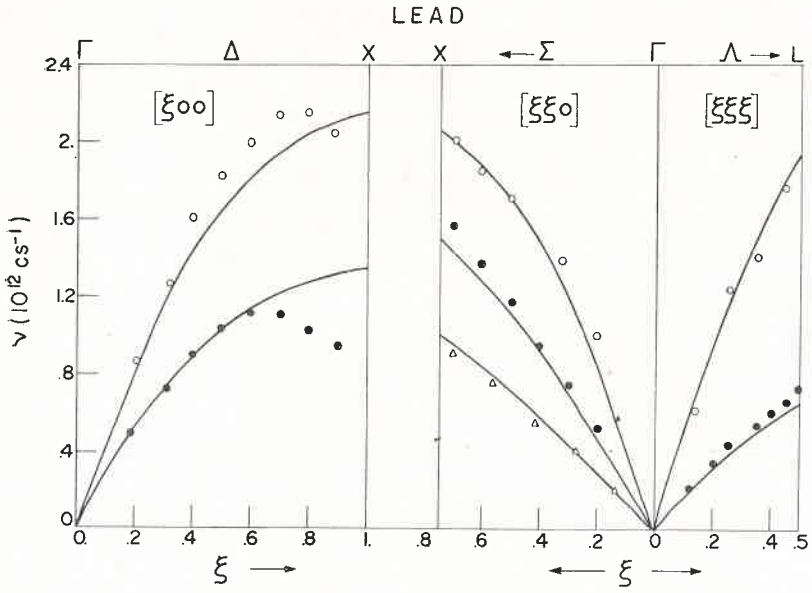

Fig. 2. Phonon dispersion relations in lead. Captions are the same as for Fig. 1

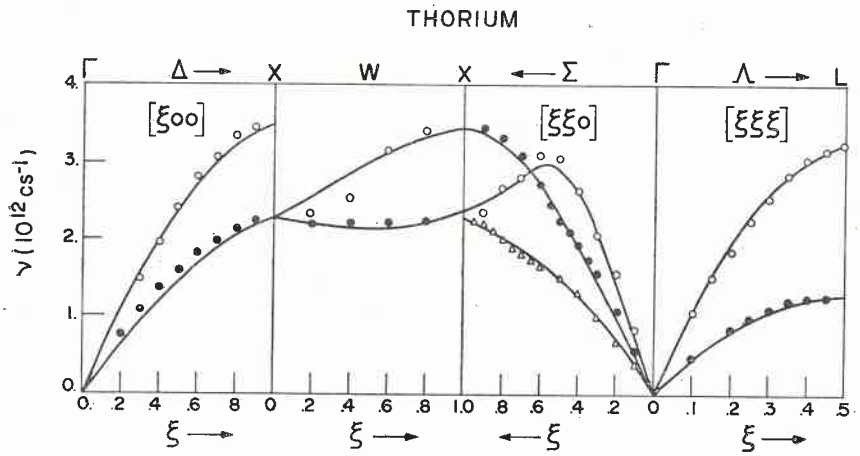

Fig. 3. Phonon dispersion relations in thorium. Captions are the same as for Fig. 1

is shown by continuous lines, experimental points are given by various symbols explained in the captions.

The calculation of specific heats of these metals has been made by a numerical sampling of the vibration spectrum. To evaluate the frequency spectrum, the entire Brillouin zone was divided into 8000 miniature cells and frequencies were calculated for the central point of each cell.

This gave rise to 24,000 frequencies. The entire frequency spectrum was divided into small intervals of width $\Delta = .05 \times 10^{12}$ Hz and the specific heat was evaluated using

Blackman's sampling technique. The calculated values of c_v were utilised to compute the $(\theta - T)$ curves of aluminium, lead and thorium and these are plotted in Figs 3 to 5 together with some experimental points for comparison purposes. The experimental c_v of aluminium and lead were taken respectively from the works of Giauque and Meads [15], and

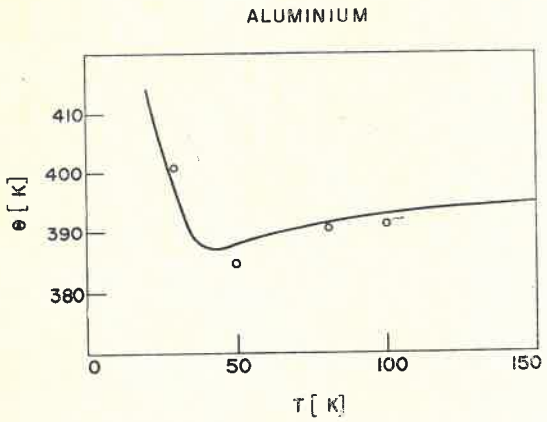

Fig. 4

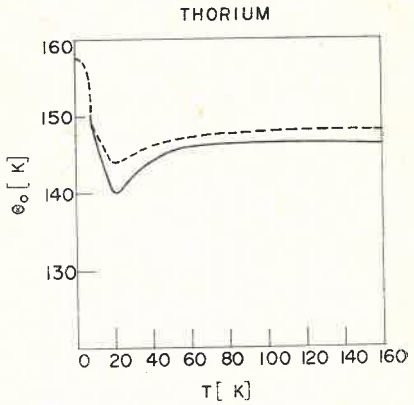

Fig. 5

Fig. 4. $(\theta$–$T)$ curves of aluminium. The theoretical curve is shown by a continuous line
Experimental points are shown by ○
Fig. 5. $(\theta$–$T)$ curves of lead. Captions are the same as for Fig. 4

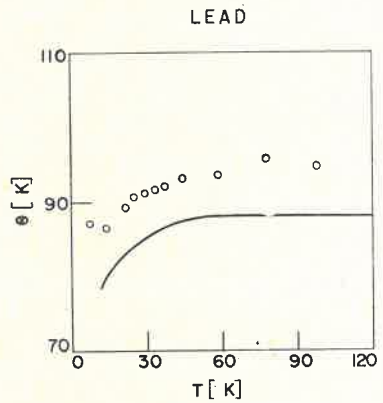

Fig. 6. $(\theta$–$T)$ curves of thorium. Captions are the same as for Fig. 4

Hoeven and Keeson [16]. For thorium the experimental c_v does not exist. In order to estimate the lattice heat capacities the coefficient of the electronic specific heat has been subtracted from the experimental c_v. This coefficient γ has the value 3.27 and 7.5 10^{-1} cal deg^{-2} mol^{-1} respectively for aluminium and thorium. These correspond to the experimental measurements of Howling et al. [17] for aluminium and that of Daunt [18] for lead.

4. Comparison with experimental results

We shall compare each metal separately.

Aluminium:

A critical study of Fig. 1 shows that the calculated phonon dispersion relation in aluminium have given an excellent account of the experimental results of Stedman and Nelsson [9]. At low vectors the two sets of results coincide. A discrepancy of the order of 6 to 8 percent exists between the calculated and experimental phonons in all symmetry directions for higher q values, especially near the zone boundaries.

The study of Fig. 4 shows that the calculated $(\theta-T)$ curve of aluminium has almost reproduced the experimental curve. The calculated curve is found to deviate at most by one percent from the experimental results.

Lead:

A close study of Fig. 2 shows that the calculated phonon dispersion curves of lead have given a very good descriptions of the experimental results. Except in region where kinks in the experimental phonons exist and here, the calculated curve deviates by 20%. The overall departure between the calculated and experimental phonons does not exceed more than ten percent.

A study of Fig. 5 shows that the calculated $(\theta-T)$ curve of lead has reproduced the entire trace of the experimental curve. The calculated curve has been found to lie about 5% below the experimental one.

Thorium:

A study of Fig. 3 implies that the calculated phonon dispersion curves of thorium along all the four principal symmetry directions have reproduced the entire trace of the experimental results. At low wave vectors the two sets of results coincide. A small discrepancy exists between the calculated and experimental phonons in the high frequency limits but such a discrepancy is found to be not more than 5%.

In the absence of experimental results, the calculated $(\theta-T)$ curve of thorium has been compared with the computed results of Reese et al. [11]. Although this comparison has not got much significance, it indicates that the two sets of results yield similar traces for the $(\theta-T)$ curve of thorium.

5. Conclusion

The lattice dynamics and heat capacities of aluminium, lead and thorium have been studied on the basis of the modified Bathia model. A critical study of the results presented here indicates that the present scheme gives a satisfactory explanation of the experimental phonon dispersion curves as well as the heat capacities of all three metals studied here. The maximum deviation between the calculated and experimental phonon frequencies of

aluminium and thorium has been found to be of the order of 8%. For lead, which is a very complicated metal with a kink existing in the experimental phonon, the deviation has been found to be of the order of 20%. The calculated and experimental θ do not differ by more than 5%. The agreements between the calculated and experimental θ could have been improved had we used zero degree values of the experimental constants for such calculations. Owing to the fact that θ does not represent an independent check of the model such calculations were not done. Also, in performing such calculations the extrapolation of the zero degree Kelvin values of the elastic constants and phonon frequencies contain lots of uncertainties. To achieve a similar kind of success the experimentalists Stedman and Nilsson [9], Miller and Brockhouse [10] and Reese et al. [11] had to employ as many as 12 to 16 free parameters. The original model of Bhatia has not been applied to the study of these metals, but certainly it would not have given this kind of result. It, thus, immerses out from the present study that the idea underlying the modification of Bhatia's model is quite justified. One can say definitely that interatomic interactions in cubic metals such as aluminium, lead and thorium, for the present case, extend at least out to the third neighbours. Similar conclusions were also drawn from earlier studies by Bertolo and Shukla [7, 8] and by Shukla and Salzberg [6].

While the original model of Bhatia [1] was linked with the Thomas-Fermi theory of electron screening, we varied such screening in all the three metals between the theories of Bohm and Pines and that of Thomas and Fermi. We came to the conclusion that the best results are obtained when the electron screening in all these three metals is considered on the theory of Bohm and Pines. For lead and aluminium definite information exists concerning the conduction electrons; but for thorium such information was missing. We, thus, assumed it to be a divalent metal and found that lattice dynamical studies of it supported this assumption.

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