

## EXTENDED DE LAUNAY MODEL STUDY OF LATTICE DYNAMICS OF ALKALI METALS

By

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The original model of de Launay has been extended to consider interionic interactions out to fourth neighbours. The present formalism has been applied to study lattice dynamics of four alkali metals viz sodium, potassium, lithium and rubidium. The phonon dispersion curves along the principal symmetry directions, frequency versus frequency distribution function as well as lattice heat capacities are calculated and compared to experimental results. An excellent agreement has been obtained between the theoretical and experimental results for all the four metals studied here.

### 1. Introduction

Before the advent of neutron inelastic scattering technique to determine experimentally the phonon wave vector versus frequency relations, a lattice dynamical model, such as that of DE LAUNAY [1] and BHATIA [2], was tested by its reproducibility of the experimental heat capacities versus Debye characteristic temperature curves. Owing to the fact that  $\Theta$  represents an averaging over the entire frequency spectrum almost all the models (see detail in DE LAUNAY [1]) were able to differ very little. It was also noticed that there was not a great need to consider interionic interactions beyond the second neighbours. Because a consideration up to second neighbours had served the purpose and also there were no experimental data to fit more distant neighbour interactions.

The availability and the interpretation of experimental dispersion curves of simple metals have revealed the fact that interatomic forces in metals are quite long ranged and thus a customary two neighbour model or three parameter model would not be able to predict extremely well the phonon dispersion relations even in the principal symmetry directions, the easiest experimental branches to fit in. It, thus, has revived a great interest in the theoretical side of lattice dynamics of simple metals.

To understand lattice dynamics of metals one needs to know the actual interatomic interactions present there. The presence and influence of conduction electrons on lattice vibrations of metals complicates the whole situation. This problem has been solved so far by two different ways. One of the methods,

which takes account of actual metallic interactions present in metals known as fundamental model, has been developed by TOYA [3] and extended further by SHAM [4], VOLSKO et al. [5], and HARRISON [6]. The other method which is much simpler in mathematical design also termed as phenomenological model has been initiated by DE LAUNAY [1] and BHATIA [2] and carried out to better and better shapes by SHARMA and JOSHI [7], KREBS [8] and CHEVEAU [9]. The models of SHARMA and JOSHI [7], KREBS [8] and that of CHEVEAU [9] have gained considerable success in the interpretation of phonon dispersion relations for several cubic metals. In some cases the original models were also modified to consider the interionic interactions beyond the second neighbours to explain the experimental results.

It was felt by the present authors that the failure of not reproducing the experimental dispersion curves of simple metals by DE LAUNAY's model [1], the first successful phenomenological model for metals, lied in its termination of interionic interactions out to second neighbours only. Recently they have thus (see SHUKLA and CAVALHEIRO [10]) extended the original model of DE LAUNAY to consider the interionic interactions out to any desired number of neighbours. They have applied their formalism to copper by calculating the phonon dispersion relations in copper and obtaining the theoretical results very close to experimental ones with interionic interactions up to fourth neighbours. The application of extended DE LAUNAY model for other f.c.c. metals (see SHUKLA and CAVALHEIRO [11]) and CAVALHEIRO and SHUKLA [12]) was also met with similar success.

The great success of extended DE LAUNAY model in the study of f.c.c. metals encouraged the present authors to take up the study of b.c.c. metals. The simple b.c.c. metals for which extensive phonon dispersion relations as well as thermal and elastic data are available are the alkali metals. We have thus computed phonon dispersion curves, lattice heat capacities and  $(\Theta - T)$  curves of these metals and these results are reported here.

## 2. Theory

The secular determinant by which the frequency of vibration is determined is given by (see SHUKLA and CAVALHEIRO [10])

$$\begin{array}{lll}
 D_{11} - m\omega^2 + pR_1 & D_{12} + qR_1 & D_{13} + rR_1 \\
 D_{21} + pR_2 & D_{22} - m\omega^2 + qR_2 & D_{23} + rR_2 = 0, \\
 D_{31} + pR_3 & D_{32} + qR_3 & D_{33} - m\omega^2 + rR_3
 \end{array} \quad (1)$$

where

$$R_1 = (D'_{11} - D_{11})p + (D'_{12} - D_{12})q + (D'_{13} - D_{13})r, \quad (2.1)$$

$$R_2 = (D'_{21} - D_{21})p + (D'_{22} - D_{22})q + (D'_{23} - D_{23})r, \quad (2.2)$$

$$R_3 = (D'_{31} - D_{31})p + (D'_{32} - D_{32})q + (D'_{33} - D_{33})r, \quad (2.3)$$

When the interionic interactions are taken up to fourth neighbours, the typical diagonal and non diagonal element of the dynamical matrix is given by:

$$D_{ii} = \frac{8}{3} \alpha (1 - C_i C_j C_k) + 4 \beta S_i^2 + 4 \gamma [1 - (2C_i^2 - 1) \cdot (C_j^2 + C_k^2 - 1)] + \\ + \frac{8}{3} \varepsilon [(11 - 9(1 - 4 S_i^2) C_i C_j C_k - 2(1 - 2 S_j^2 - 2 S_k^2) C_i C_j C_k), \quad (3.1)$$

$$D_{ij} = \frac{8}{3} \alpha C_k S_i S_j + 8 \gamma C_i S_i S_j + \frac{8}{11} \varepsilon [6(2 C_i^2 + 2 C_j^2 - 1) + (1 - 4 S_k^2)] C_k S_i S_j, \quad (3.2)$$

$$S = \sin a K_i,$$

$$C = \cos a K_i.$$

$a$  = lattice parameter and  $K_i (i = 1, 2, 3)$  are cartesian components of the wave vector  $\vec{k} \cdot p, q$  and  $r$  are the direction cosines of wave vector  $\vec{k}$ .

By changing  $\alpha, \beta, \gamma, \varepsilon$  to  $\alpha', \beta', \gamma', \varepsilon'$ , the elements  $D'_{ii}$  and  $D'_{ij}$  are obtained from (3.1) and (3.2).

### 3. Relation between elastic constants and force constants

By expanding the secular determinant in long wavelength limits the following relation between elastic constants and force constants are obtained

$$ac_{11} = \frac{2}{3} \alpha' + 2 \beta' + 4 \gamma' + \frac{166}{11} \varepsilon', \quad (4.1)$$

$$ac_{12} = 2 \alpha' + 6 \gamma' + \frac{114}{11} \varepsilon' - \frac{4}{3} \alpha - 4 - \frac{11}{76} \varepsilon, \quad (4.2)$$

$$ac_{44} = \frac{2}{3} \alpha + 2 \gamma + \frac{38}{11} \varepsilon \quad (4.3)$$

with the following interrelation among the force constants

$$2(\alpha' - \alpha) + 3(\gamma' - \gamma) = 3(\beta' - \beta) + \frac{78}{11}(\varepsilon' - \varepsilon). \quad (4.4)$$

The bulk modulus of electron gas is given by

$$Ke = C_{12} - C_{44} = \frac{2}{a}(\alpha' - \alpha) + 3(\gamma' - \gamma) + \frac{57}{11}(\varepsilon' - \varepsilon) \quad (4.5)$$

#### 4. Phonon dispersion relations along symmetry directions

In these directions the solution of dynamical matrix reduces to very simple equations such as:

$$m\omega_{Lq0}^2 = D'_{11}, \quad (5.1)$$

$$m\omega_{Tq0}^2 = D_{11} + D_{12}, \quad (5.2)$$

$$m\omega_{Lqq}^2 = D'_{11} + D'_{12}, \quad (5.3)$$

$$m\omega_{Tqq}^2 = D_{11} - D_{12}, \quad (5.4)$$

$$m\omega_{Tqq}^2 = D_{33}, \quad (5.5)$$

$$m\omega_{Lqq}^2 = D'_{11} + 2D'_{12}, \quad (5.6)$$

$$m\omega_{Tqq}^2 = D_{11} - D_{12}. \quad (5.7)$$

#### 5. Lattice specific heat calculations

The calculation of lattice specific heat can be carried out on the basis of the formula

$$C_v = 3R \int_0^{\nu_L} E(h\nu/KT) g(\nu) d(\nu), \quad (6.1)$$

where  $g(\nu)$  is the frequency distribution function and  $E(x)$  is the Einstein specific heat function given by

$$E(x) = \frac{x^2 e^x}{(e^x - 1)^2}, \quad (6.2)$$

where  $\nu_L$  is the largest frequency in the frequency spectrum and  $R$  is gas constant.

## 6. Numerical computations

Before the calculation of phonon frequencies is carried out the evaluation of numerical values of force constants is necessary. There are seven independent parameters in this model and we needed seven independent equations to determine them numerically. We have used three equations relating the force constants with elastic constants and four more equations relating the force constants with the experimental zone boundary frequencies of the first Brillouin zone. We made several choices of these four frequencies and found that the zone boundary frequencies corresponding to  $|\xi 00|$  and  $|\xi \xi 0|$  branches gave good fit with the experimental dispersion curves. Care was taken to use the experimental elastic constants either at the temperature at which phonon frequencies were measured or very near to that very temperature. The phonon frequencies of sodium were measured by WOODS et al. [13] at 90 °K but the experimental values of elastic constants were available only at 78 °K. Thus we had to employ 78 °K values of elastic constants from the work of QUIMBY and SIEGEL [14].

The phonon frequencies of potassium were measured by COWLEY et al. [15] at 9 °K but no experimental values of elastic constants were available at that temperature. We thus took the values of elastic constants at 4.2 °K from the work of MARQUARDT and TRIVISONNO [16]. The phonon frequencies of lithium were measured at 98 °K in the work of SMITH et al. [17]. In the absence of elastic constant data at that temperature we took the values of elastic constants at 78 °K from the work of NASH and SMITH [18]. The phonon frequencies of rubidium were measured at 120 °K by COPLEY et al. [19]. The experimental value of elastic constants of this metal was available only at 80 °K from the work of ROBERTS and MEISTENER [20]. Then set of 80 °K elastic constants did not give a good fit with experimental results. We then used the extrapolated values of elastic constants at 120 °K from the work of COPLEY et al. [19]. Even that also did not give a good fit. COPLEY et al. [19] had put some doubt on the experimental value of  $c_{11}$ . We thus varied the values of  $c_{33}$  arbitrarily and found that about 8% a higher value of  $c_{11}$  than predicted by COPLEY et al. [19] gave excellent fit with the experimental data. Our choice of  $c_{11}$  was quite close to that predicted theoretically by BAILYN (see HUNTINGTON [21]). The input data to calculate force constants are given in Table I, while the output values of force constants are given in Table II. The calculation of phonon dispersion curves along the three principle symmetry directions has been carried out on the basis of equation number 5.1 to 5.7. The calculated phonon dispersion curves of sodium, potassium, lithium and rubidium are shown in Figures 1 to 12 together with experimental points for comparison. The specific heats at constant volume have been calculated on the basis of Blackman's sampling technique. For this purpose we divided the first Brillouin

**Table I**  
Input data to calculate force constants

Substance	Elastic Constants			Atomic Mass $10^{-23}$ gm	Lattice Parameter ( $10^{-8}$ cm)	Phonon Frequencies (THz)
	$C_{11}$ ( $10^{11}$ dyn $\text{cm}^{-2}$ )	$C_{12}$ ( $10^{11}$ dyn $\text{cm}^{-2}$ )	$C_{44}$ ( $10^{11}$ dyn $\text{cm}^{-2}$ )			
Sodium	.808	.664	.586	3.8163	4.24	$\nu_{L_{100}} = 3.58$ $\nu_{T_{100}} = 3.58$ $\nu_{L_{110}} = 3.82$ $\nu_{T_{110}} = 2.56$
Potassium	.4167	.3413	.2860	6.4909	5.225	$\nu_{L_{100}} = 2.21$ $\nu_{T_{100}} = 2.21$ $\nu_{L_{110}} = 2.40$ $\nu_{T_{110}} = 1.50$
Lithium	1.484	1.253	1.080	1.1520	3.491	$\nu_{L_{100}} = 8.82$ $\nu_{T_{100}} = 8.82$ $\nu_{L_{110}} = 9.00$ $\nu_{T_{110}} = 5.70$
Rubidium	3.26	2.78	1.57	14.188	5.620	$\nu_{L_{100}} = 1.315$ $\nu_{T_{100}} = 1.315$ $\nu_{L_{110}} = 1.460$ $\nu_{T_{110}} = .900$

zone into an evenly spaced sample of 1000 wavevectors. From the symmetry requirements these 1000 points were reduced to only 47 nonequivalent points including the origin, lying within 1/48th part of the Brillouin zone. After solving the secular determinant for these 47 points, the specific heats were calculated with the help of equation 10.1. There are several data for the experimental  $C_v$  for all the alkali metals. The experimental heat capacities of sodium were measured by MARTIN [22], SIMON and ZEIDLER [23], FILBY and MARTIN [24], ROBERTS [25] and PARKINSON and QUARRINGTON [26]. For comparison with our theoretical results we have chosen the experimental results of MARTIN [22] and that of SIMON and ZEIDLER [23] because these measurements covered a wide temperature range of  $C_v$ . The experimental value

**Table II**

Substance	$\alpha$	$\beta$	$\gamma$	$\epsilon$	$\alpha$	$\beta$	$\gamma$	$\epsilon$
Sodium	3700	472	111	-29.0	3580	213	27.3	11.1
Potassium	2430	437	35.0	-30.5	2230	48.3	-61.5	36.3
Lithium	6550	690	-245	27.5	6470	464	-364	52.3
Rubidium	1900	420	52.3	-31.0	1880	292	-38.2	-22.4

of  $\gamma$ , the electronic heat capacity coefficient for sodium was taken to be  $330\mu$  cal deg<sup>-2</sup> mol<sup>-1</sup> from the work of MARTIN [27]. The lattice heat capacities of potassium were measured by SIMON and ZEIDLER [23], KRIER et al [28], ROBERTS [25], FILBY and MARTIN [24] and LIEN and PHILLIPS [29]. To compare with our theoretical  $C_v$  we have chosen the results of KRIER et al [28] and that of FILBY and MARTIN [24] as they covered a wide temperature range of  $C_v$ . The coefficient of electronic heat capacity for potassium was taken to be  $497\mu$  cal deg<sup>-2</sup> mol<sup>-1</sup> from the work of FILBY and MARTIN [30]. The experimental heat capacities of lithium were measured by SIMON and SWAIN [31], MARTIN [32], FILBY and MARTIN [24] and by ROBERTS [25]. The most reliable set of experimental results were those of MARTIN [32] and that of SIMON and SWAIN [31]. We have compared our theoretical  $C_v$  with these data. The coefficient of electronic heat capacity for lithium was taken from the measurement of MARTIN [33]. The lattice heat capacities of rubidium were measured by LIEN and PHILLIPS [29], FILBY and MARTIN [24] and by MANCHESTER [34]. The results of FILBY and MARTIN were chosen for comparison with our theoretical  $C_v$  as this covers a wide temperature range of experimental data of  $C_v$ . The coefficient of electronic heat capacity for rubidium was taken from the measurements of FILBY and MARTIN [30]. The calculated and experimental  $C_v$  versus temperature curve for all alkali metals are shown in Fig. 13. The calculation of Debye characteristic temperature,  $\Theta$ , follows from the knowledge of the heat capacities and the temperature at which such calculations were made. The corresponding  $(\Theta - T)$  curves of all the four alkali metals are shown in Figs. 14 to 17 together with experimental curves for comparison.

## 7. Comparison with experimental results

### A. Sodium

The study of Figs. 1 to 3 shows that there is an excellent agreement between the calculated and experimental phonon frequencies for all the three symmetry directions. Some little deviations exist in the transverse branches of  $|\xi\xi\xi|$  and  $|\xi\xi0|$  but, in no case do these deviations amount to more than 3 percent. The study of Fig. 13 reveals that the theoretical  $C_v$  has almost reproduced the experimental ones in the temperature range of 0° to 250 °K. The study of Fig. 14 indicates that the theoretical  $(\Theta - T)$  curve has reproduced the entire course of the experimental curve but it lies about two percent below the experimental curve. The theoretical curve showed good agreement with the experimental results of SIMON and ZEIDLER [23] at higher temperatures and with the results of FILBY and MARTIN [24] at low temperatures.

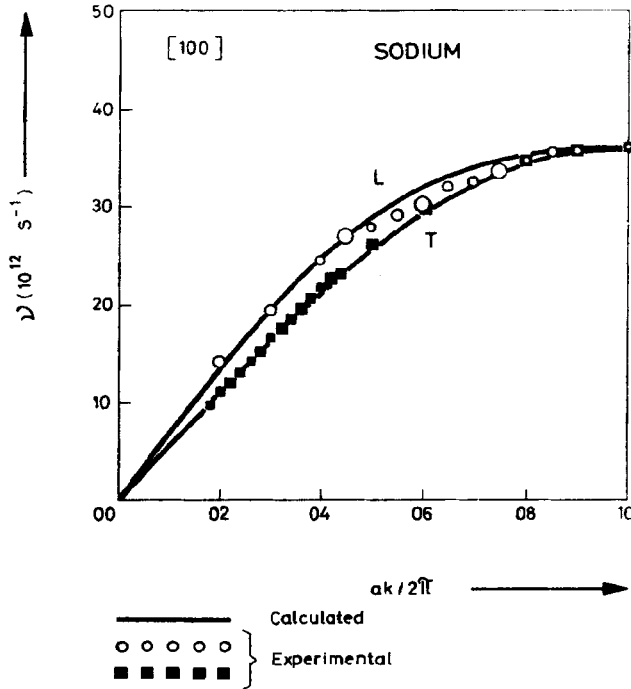


Fig. 1. Dispersion curves of sodium along [100] direction. Experimental data of Woods et al. marked by ■ and ○. The small or big symbols for the same branch are adapted to show the corresponding uncertainties in the experimental frequency

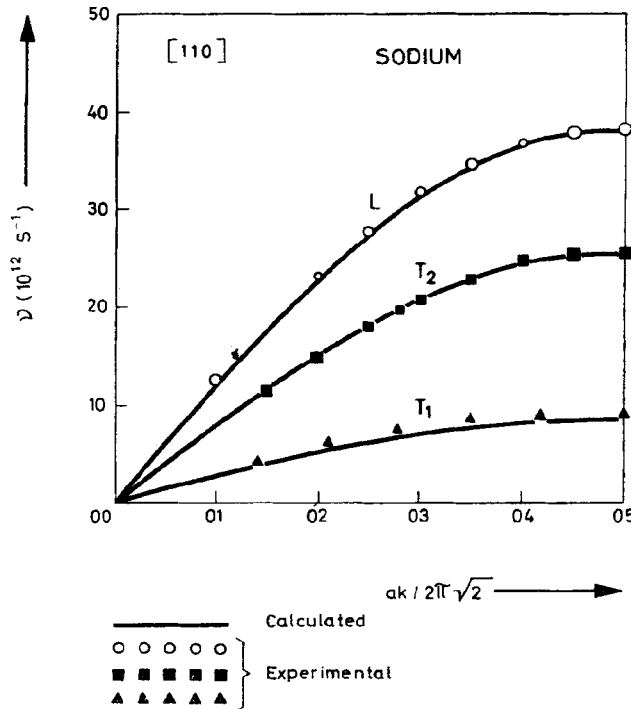


Fig. 2. Dispersion curves of sodium along [110] direction. Captions are the same as for Fig. 1. Two experimental transverse branches are marked by ■ and ▲



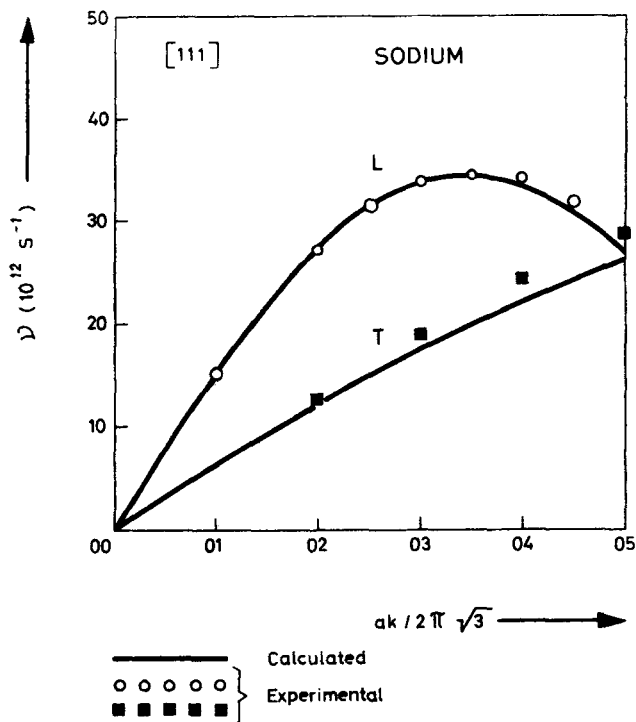


Fig. 3. Dispersion curves of sodium along [111] direction. Captions are the same as for Fig. 1

### B. Potassium

A study of Figs. 4 to 6 reveals the fact that there is an excellent agreement between the calculated and experimental phonon dispersion relations of potassium along all the three principal symmetry directions. Probably, a noticeable difference between the theoretical and experimental result is exhibited in the transverse branch of  $|\xi\xi\xi|$  and, that too, in the high frequency ends only. The maximum departure between the calculated and experimental frequency has been found to be of the order of four percent. No comparison was possible for the transverse branch  $T_1$  of the  $|\xi\xi 0|$  direction as no experimental data exist for this branch. From the study of Fig. 13 one can make out that there is excellent agreement between the calculated and experimental heat capacities. The calculated curve has almost reproduced the experimental ones in the whole temperature range of 0 °K to 150 °K. An inspection of Fig. 15 gives an idea that the calculated  $(\Theta - T)$  curve is in excellent agreement with the experimental curve. The calculated curve is on the average about two percent below the experimental curve. The agreement towards the higher temperature region is much better.

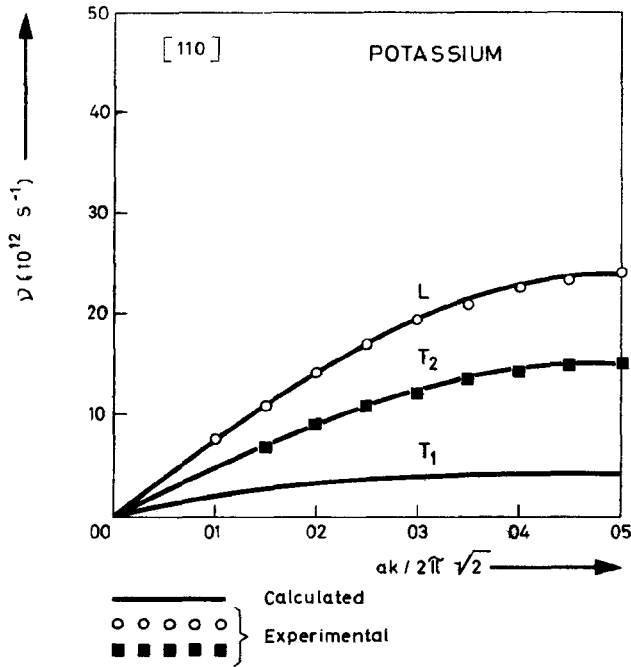


Fig. 4. Dispersion curves of potassium along [100] direction. Experimental data of COWLEY et al. marked by ○ and ■. The small or big symbols for the same branch are adapted to show the corresponding uncertainties in the experimental frequency

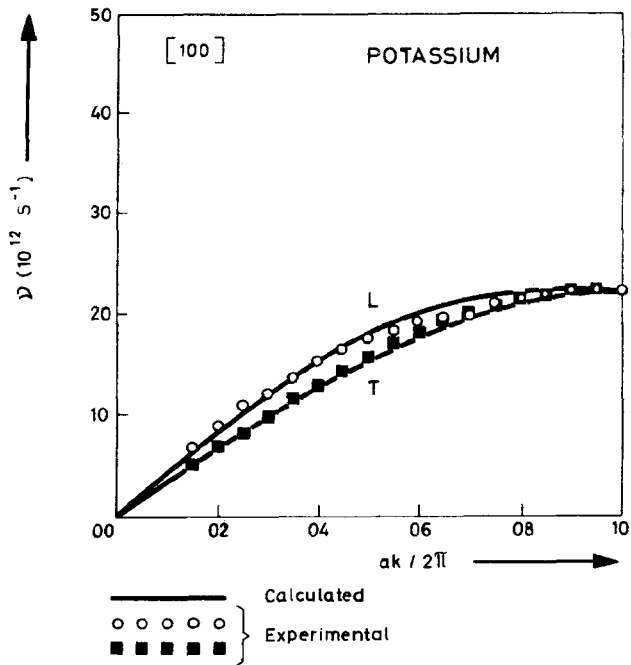


Fig. 5. Dispersion curves of potassium along [110] direction. Captions are the same as that of Fig. 4

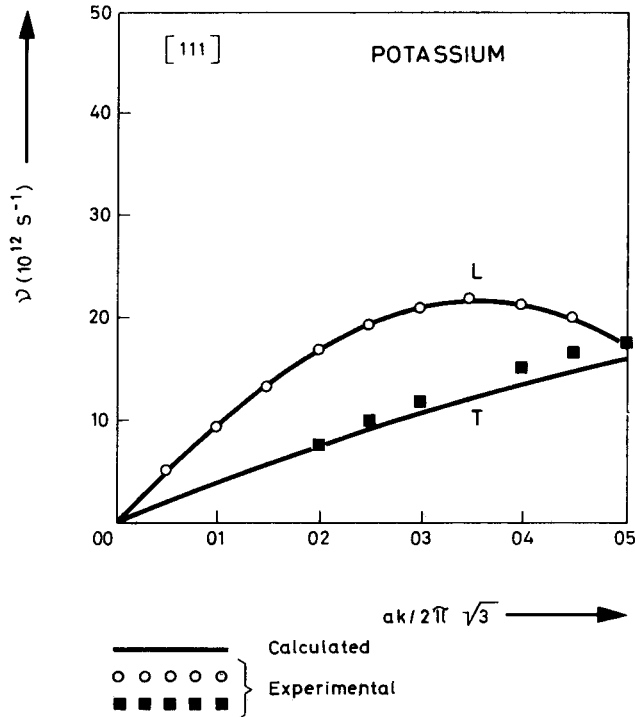


Fig. 6. Dispersion curves of potassium along [111] directions. Captions are the same as that of Fig. 4

### C. Lithium

A study of Figs. 7 to 9 reveals the fact that there is an excellent agreement between the calculated and experimental dispersion relations of lithium in all the symmetry directions. The experimental error in the measurements of experimental phonon frequencies of this metal has been maximum in comparison to other alkali metals. Since we have fitted the force constants with the experimental zone boundary frequencies the uncertainty in the calculated force constants was impossible to eliminate. Seeing all this ambiguity the agreement between the calculated and experimental phonon frequencies is remarkable. The theoretical curve was unable to explain the crossing of transverse and longitudinal branches in the  $[\xi 00]$  direction. The maximum difference between the calculated and experimental phonon frequency is found to be less than five percent. A study of Fig. 13 shows that the theoretical  $C_v$  versus temperature curve shows an excellent agreement with the experimental curve. The theoretical curve is found to be above the experimental curve up to 180 °K and above that it lies atop the theoretical curve. A study of Fig. 16 reveals that the theoretical  $(\Theta - T)$  curve of lithium has been able to reproduce the entire

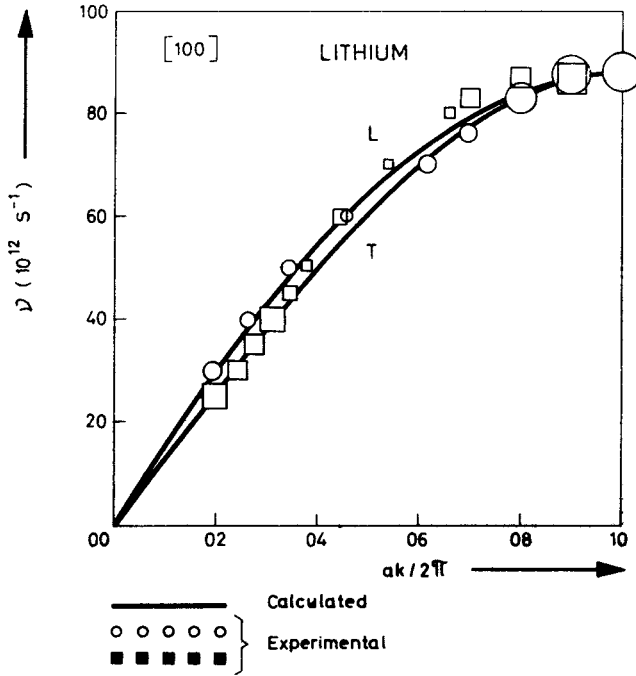


Fig. 7. Dispersion curves of lithium along [100] direction. Experimental data of SMITH. et al. marked by ○ and □. The small or big symbols for the same branch are adapted to show the corresponding uncertainties in the experimental frequencies

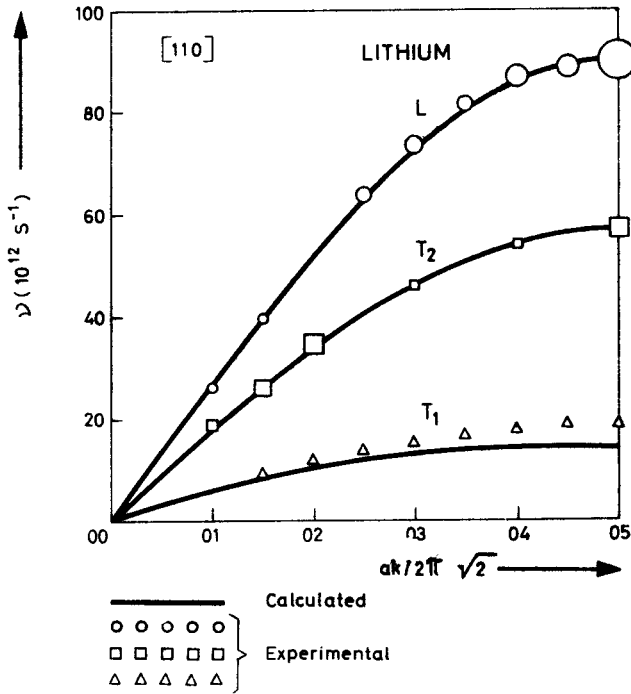


Fig. 8. Dispersion curves of lithium along [110] direction. Captions are the same as that of Fig. 7 except that there is one more experimental transverse branch marked by △

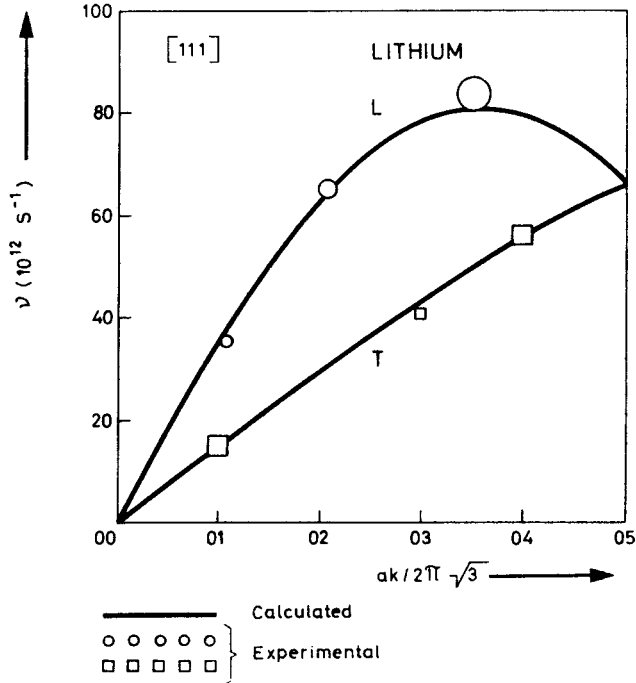


Fig. 9. Dispersion curves of lithium along [111] direction. Captions are the same as that of Fig. 7

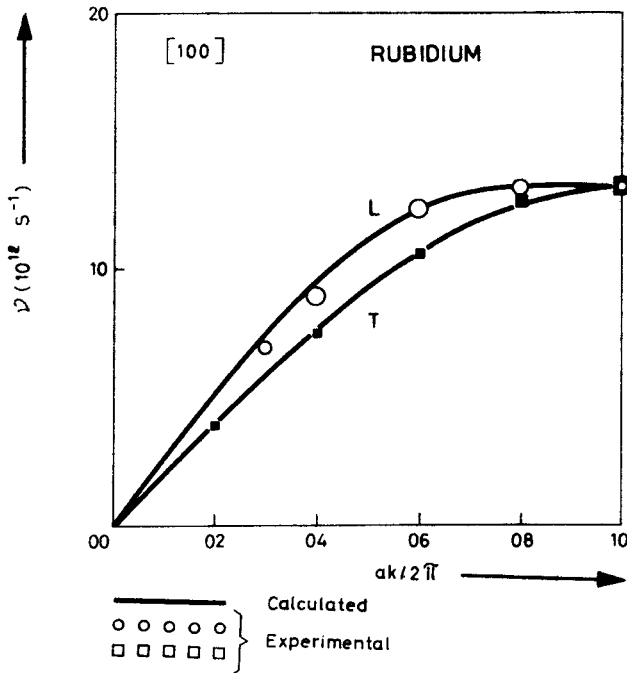


Fig. 10. Dispersion curves of rubidium along [100] direction. Experimental data of COPLEY et al. are marked by ○ and ■. The small or big symbol for the same branch are adapted to show the corresponding experimental uncertainties

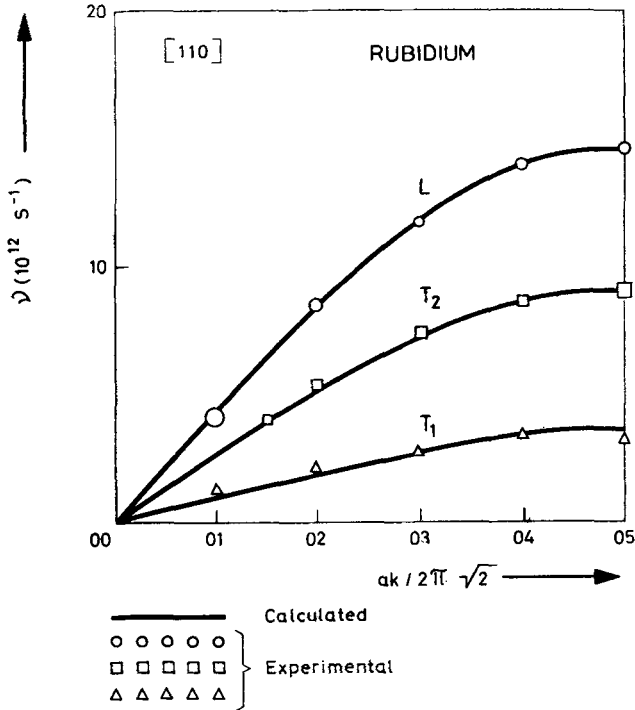


Fig. 11. Dispersion curves of rubidium along [110] direction. Captions are the same as that for Fig. 10. The two experimental transverse branches are shown by □ and △

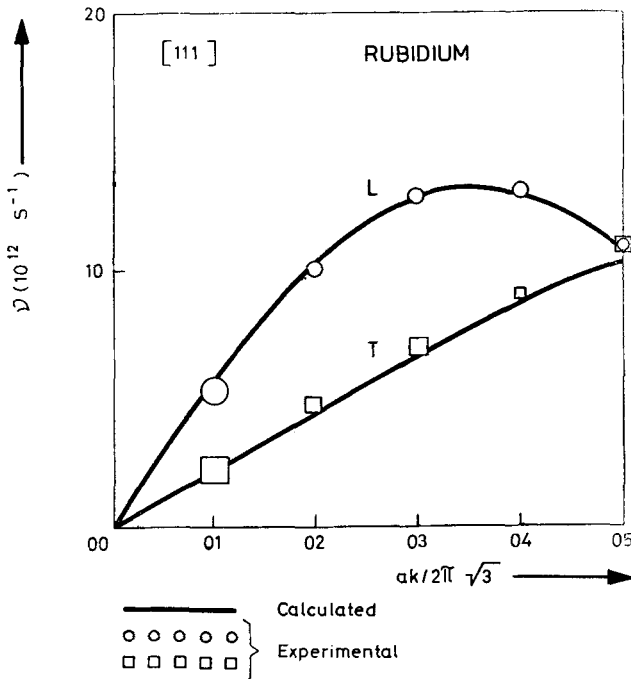


Fig. 12. Dispersion curves of rubidium along [111] direction. Captions are the same as that for Fig. 10

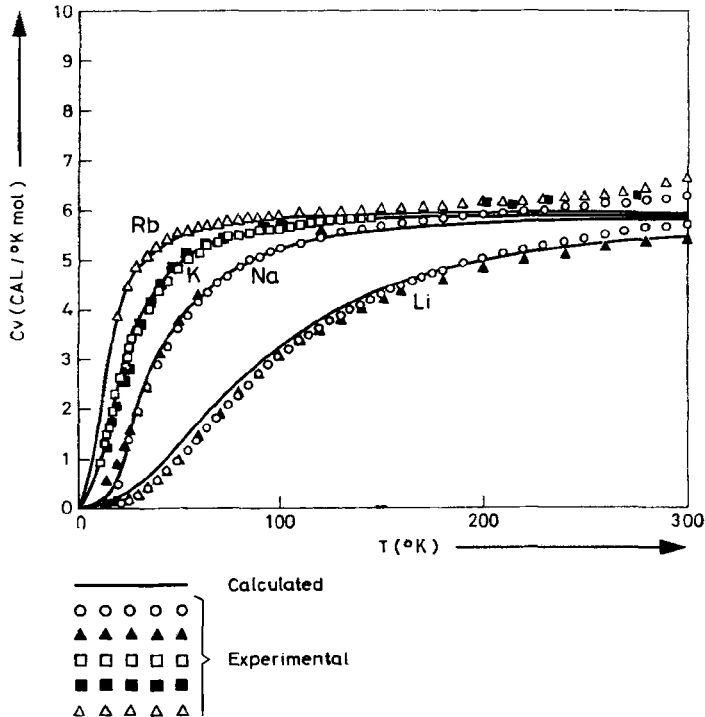


Fig. 13. Lattice heat capacities versus temperature curves of sodium, potassium, lithium and rubidium. While the calculated curves are shown by solid lines the experimental points of FILBY and MARTIN, SIMON and SWAIN, PARKINSON and QUARRINGTON, SIMON and ZEIDLER and KRIER et al. are shown by □, □, ■, ▲, and △ respectively

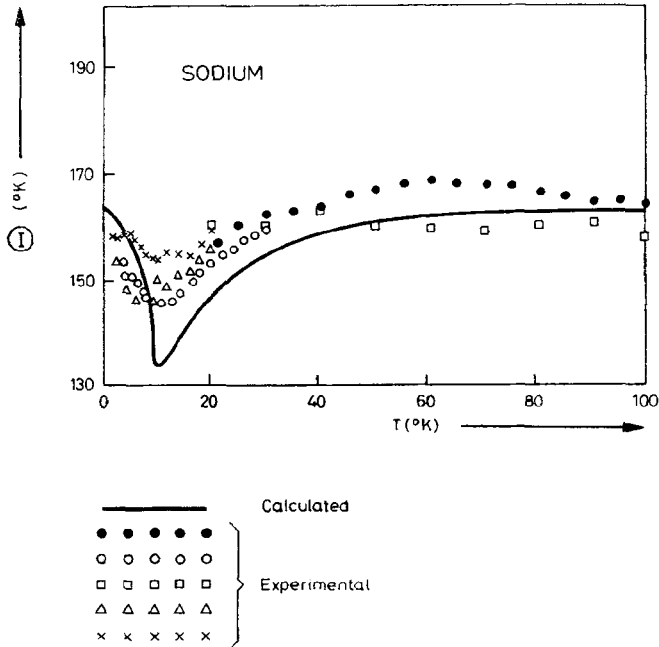
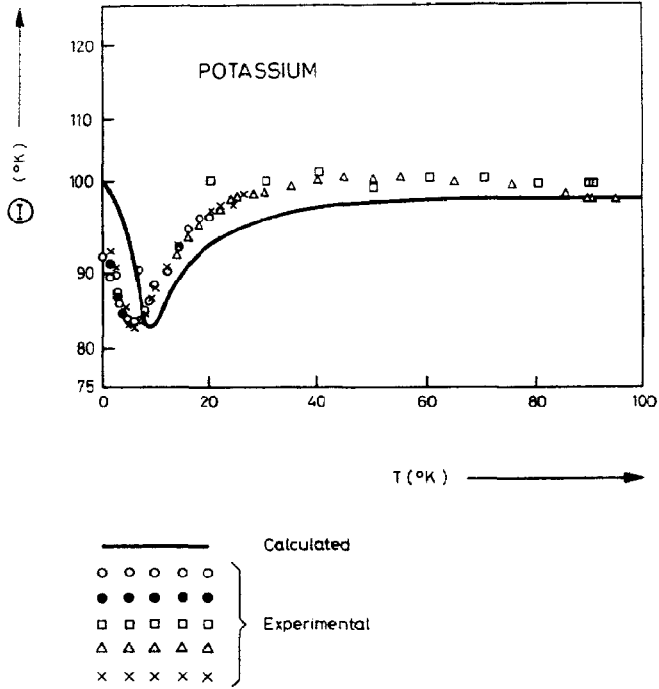
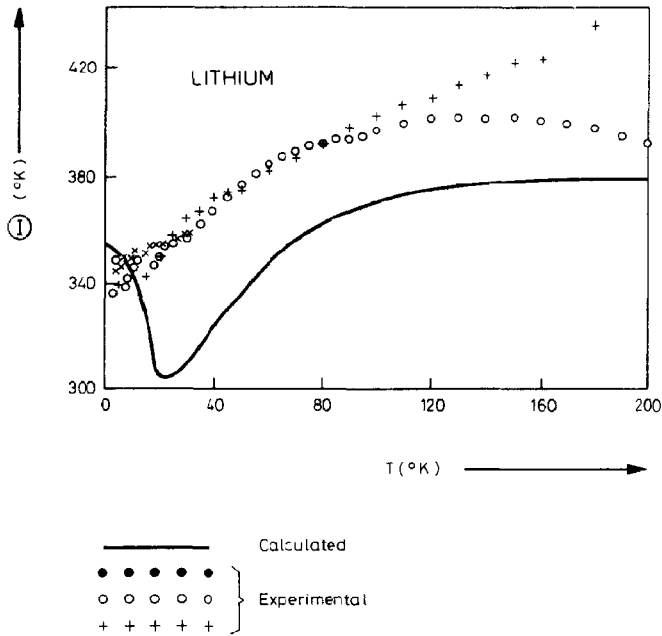


Fig. 14.  $(\theta-T)$  curves of sodium. The experimental points from the measurements of ROBERTS, PARKINSON and QUARRINGTON, FILBY and MARTIN, MARTIN and SIMON and ZEIDLER are marked by X, △, ○, ● and □ respectively

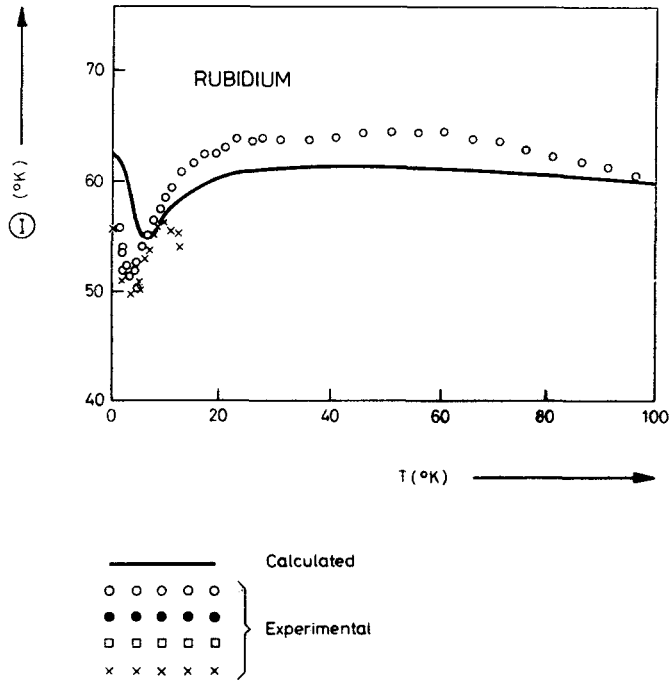


**Fig. 15.**  $(\theta-T)$  curves of potassium. The experimental points from the measurements of FILBY and MARTIN, KRIER et al., ROBERTS, LIEN and PHILLIPS and SIMON and ZEIDLER are shown by X,  $\Delta$ ,  $\bullet$ ,  $\circ$  and  $\square$  respectively



**Fig. 16.**  $(\theta-T)$  curves of rubidium. The experimental points from the measurements of FILBY and MARTIN, MCCOLLUM and SILSBEE, LIEN and PHILLIPS and MANCHESTER are shown by  $\circ$ , X,  $\bullet$ ,  $\square$  and + respectively





*Fig. 17.*  $(\theta - T)$  curves of lithium. The experimental points from the measurements of FILBY and MARTIN, MARTIN, ROBERTS and SIMON and SWAIN are shown by X, ○, ◆ and + respectively

shape of the experimental curve but the theoretical curve lies about 4% below the experimental curve. The agreement between the two results seems to be better in the regions of low temperature range than in that of high temperature range.

#### D. Rubidium

A study of Figs. 10 to 12 reveals the information that the theoretical phonon frequencies of rubidium have almost reproduced the experimental ones. Very little deviations exist between the calculated and experimental phonon frequencies in the transverse branch of  $[\xi\xi0]$  and also near the zone boundary in the  $[\xi\xi\xi]$  direction. A study of Fig. 13 reveals that the theoretical heat capacities are in excellent agreement with the experimental results. The theoretical  $C_p$  curve has almost reproduced the experimental curve up to a temperature of 180 °K and above that the theoretical curve attains saturation and the experimental curve rises further. A study of Fig. 17 shows that the theoretical  $(\theta - T)$  curve has reproduced the correct shape of the experimental curve. The theoretical curve lies about two percent below the ex-

perimental curve. The agreement between the calculated and experimental  $\Theta$  has been found to be much better in the high temperature range.

### 8. Discussion

The present study of lattice dynamics of four alkali metals, namely that of sodium, potassium, lithium and rubidium, on the basis of extended DE LAUNAY's model has given an excellent agreement between the calculated and experimental phonon dispersion relations along the most symmetric directions, lattice heat capacity versus temperature curve and Debye characteristic temperature versus temperature curve. The agreement between theoretical and experimental results have been extremely good and in most of the cases the theoretical results have almost reproduced the experimental ones. The maximum deviation between the two sets of results have been found of the order of 3% in the case of phonon frequencies and of the order of 4% in the case of Debye characteristic temperature. It should be pointed out that the original DE LAUNAY model applied to alkali metals had failed to reproduce the experimental phonon frequencies and was also not able to give such a good agreement between theoretical and experimental  $\Theta$  as can be seen from the works of DAYAL and SHARAN [35, 36]. The application of extended DE LAUNAY's model to f.c.c. structure, as is evident from the works of SHUKLA and CAVALHEIRO [10, 11] and CAVALHEIRO and SHUKLA [12], also met with a similar success. Thus the study of lattice dynamics of several simple cubic metals on the basis of extended DE LAUNAY's model has confirmed this point that inter-ionic interactions in metals are quite long ranged and at least fourth nearest neighbour interactions are necessary to obtain a good fit with the experimental lattice dynamical data.

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