LATTICE DYNAMICS OF ALUMINIUM AND THORIUM*

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Phonon dispersion relations along the three principal symmetry directions as well as the (θ–T) curves of aluminium and thorium have been calculated on the basis of a model proposed by us. In the model, the ion-ion interaction term from the axially symmetric model of Lehman et al. and the electron-ion interaction of Krebs were combined. Computed results are in close agreement with experimental findings.

1. Introduction

Lattice dynamics of metals has been a subject of considerable study for the past few decades. Earlier attempts were only confined to predicting and interpreting the variation of the Debye temperature. The Debye temperature is not a sure index of the validity of a model. As it does not depend on a single phonon frequency, but on an average over the entire phonon spectrum, all models gave almost similar results (see for example Cocharan [1], de Launey [2] and Joshi and Rajagopal [3]). The advent of thermal neutron spectroscopy has been responsible for the availability of experimental phonon frequencies of several cubic metals. Interpretation of their phonon dispersion curves has shown that in spite of the great efforts by theoreticians to develop successful models for metals, we are still far from the true picture. To develop a theoretical model one is beset with the difficulty to propound the exact dependence of the interatomic interactions holding the solid together. To date, there exist only two different approaches. In one of these methods, classical equations of motions are set up to determine the vibrational frequencies of atomic ions. The effect of conduction electrons are introduced on a phenomenological basis. Models developed along these lines are known phenomenological models. In the other approach, interatomic interactions are split up into a more exact formalism i. e. Coulomb interaction between the charges holding the two atoms together, overlap repulsion keeping the two atoms apart and the electron-ion-electron interaction from perturbation theories.

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Models along these lines are known as first principle models. It is necessary here to point out that the phenomenological models are very simple in mathematical formalism and require less computational labour than the first principle models. This is why there exists numerous phenomenological models. A look at the recent past may reveal that out of all models developed so far, the models which take into account the lattice periodicity are found to explain better the dependence of phonon frequencies on wave vectors (see for example Shukla [4], Shukla et al. [5], Shukla and Closs [6], Singh and Sharma [7] and Krebs [8]). The modified axially symmetric model proposed by Shukla et al. [5, 6] has been found to give better results than other existing models. The great success of this model for noble metals has encouraged us to study aluminium and thorium on its basis. These two metals were studied because they are both non-monovalent metals. Aluminium is a trivalent metal and thorium a divalent one. For aluminium, extensive data on experimental phonon dispersion curves have existed for quite some time and for thorium such measurements have been carried out quite recently. For both of them exists much eleastic and thermal data to facilitate lattice dynamical studies.

2. *Theory*

The phonon frequencies are given by the solution of the secular determinant

$$|D_{\alpha\beta}(q) - m\omega^2 \mathrm{I}| = 0,$$

where: $D_{\alpha\beta}(q)$ is the dynamical matrix, m is the ionic mass, ω is the angular frequency, I is a unit matrix of order 3.

Each element of the dynamical matrix $D_{\alpha\beta}$ is split up into two parts i. e. an ion-ion interaction part, $D^{ii}_{\alpha\beta}(q)$ and an electron-ion interaction part, $D^{ie}_{\alpha\beta}(q)$. The ion-ion interaction part of the dynamical matrix has been taken from the work of Lehman et al. [9]. The electron-ion interaction has been taken from the work of Krebs [8].

The typical diagonal and non-diagonal parts of the dynamical matrices are given by:

$$D^{ii}_{ii}(q) = 4A_1(3 - C_iC_j - C_jC_k - C_kC_i) + 2B_1[(2 - C_i(C_j - C_k)] + 2A_2[3 - C_{2i} - C_{2j} - C_{2k}]$$

$$+ 2B_2(1 - C_{2i}),$$

$$D^{ie}_{ij} = 2B_1 S_i S_j,$$

$$D^{ie}_{ii} = \frac{a^3\lambda^2 K_e}{4} \sum_h \left[\frac{(q_i + h_i)^2 G^2(u_1)}{(q+h)^2 + \frac{a^2\lambda^2}{4\pi^2} f(t_1)} - \frac{h_i^2 G^2(u_2)}{h^2 + \frac{a^2\lambda^2}{4\pi^2} f(t_2)} \right],$$

$$D^{ie}_{ij} = \frac{a^3\lambda^2 K_e}{4} \sum_h \left[\frac{(q_i + h_i)(q_j + h_j) G^2(u_1)}{(q+h)^2 + \frac{a^2\lambda^2}{4\pi^2} f(t_1)} - \frac{h_i h_j G^2(u_2)}{h^2 + \frac{a^2\lambda^2}{4\pi^2} f(t_2)} \right],$$

where A_i, B_i are the axially symmetric force constants for the i^{th} neighbour, S_i and C_i are respectively sin (πaki) and cos (πaki) $(i = 1, 2, 3)$ and a is the lattice parameter. λ is the screening parameter given by:

$$.353\left(\frac{r_s}{a_0}\right)^{1/2} K_F < \lambda < .814\left(\frac{r_s}{a_0}\right)^{1/2} K_F,$$

where K_F is the Fermi wave vector, a_0 is the Bohr radius, r_s is the radius of the atomic sphere.

The functions $f(t)$ and $g(u)$ are the same as given in Krebs' [8] paper. By expanding the secular determinant in the long wavelength limit $(q \to 0)$ the relations between force constants and elastic constants are given by:

$$aC_{11} = 4A_1+2B_1+4A_2+4B_2+aK_e, \quad aC_{12} = B_1-4A_1-4A_2+aK_e,$$
$$aC_{44} = B_1+4A_1+4A_2.$$

3. *Numerical computations*

The first step in the numerical computation is the evalution of the force parameters. To evaluate uniquely all five parameters, five independent equations were used: three relating the force constants and elastic constants, and two the phonon frequencies from the boundary of the Brillouin zone.

Care was taken to utilise the values of the elastic constants at the same temperature at which the phonon frequencies were measured. The phonon frequencies of aluminium were measured at 80°K by Stedman and Nilsson [10]. The phonon frequencies of thorium were measured by Reese et al. [11] at room temperature. We, thus, took the 80°K values of the elastic constants of aluminium from the work of Kamm and Allers [12] and took the room temperature values of thorium from the work of Mac Farlane et al. [13]. We

TABLE I

Input data to calculate the force constants

Metal	Lattice constant 10^{-8} cm (a)	Elastic constants 10^{11} dyn/cm^2 $(c_{11}$	c_{12}	$c_{44})$	Atomic mass 10^{-23} gm (M)	Phonon frequencies 10^{12} Hz $\nu_{L\xi 00}$	$\nu_{T\xi\xi\xi}$
Aluminium	4.0251	11.373	6.191	3.128	4.48	9.68	9.64
Thorium	5.0843	7.53	4.89	4.78	38.53	3.47	2.26

TABLE II

Calculated values of the force constants 10^3 dyn/cm

Metal					
Thorium	31.24	−.986	−2.592	.858	13.31
Aluminium	34.02	7.42	−3.03	−2.33	−30.53

made different choices of the zone boundary frequencies for aluminium and thorium but found that the longitudinal zone boundary frequency from the [100] and the transversal zone boundary frequency from the [111] directions gave the best results. We also tested several choices of the screening parameter by varying the numerical constants between the limits .353 to .814. We found that the choice of .353 gave the best results. Numerical values of input data are given in Table I. Output values of the force constants are given in Table II. Calculated phonon dispersion curves of aluminium and thorium are plotted

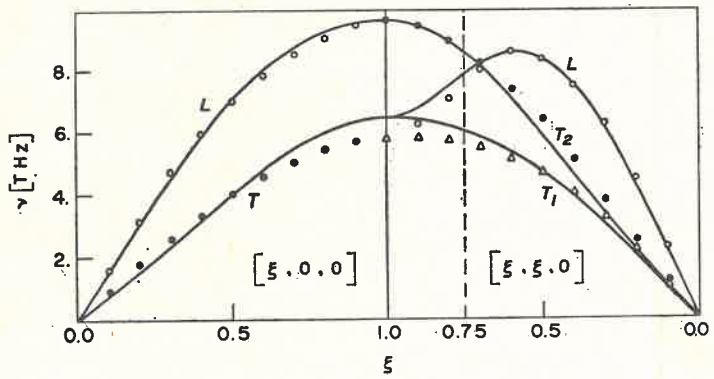

Fig. 1. Phonon dispersion relations in aluminium along the $|\xi 00|$ and $|\xi\xi 0|$ directions. While calculated curves are shown by continuous lines, experimental points are given by ○, ●, and Δ

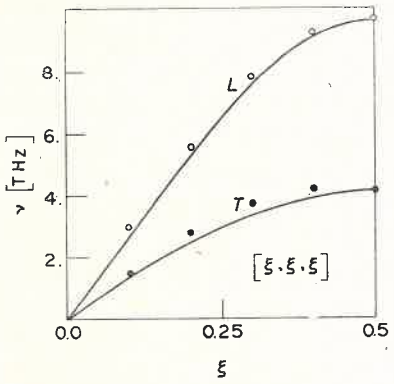

Fig. 2. Phonon dispersion relations in aluminium along the $|\xi\xi\xi|$ direction. Captions are the same as for Fig. 1

in Figs 1 to 4 together with experimental points for comparison purposes. While the theoretical curves are shown by continuous lines, experimental points are shown by the various symbols explained in the captions.

In order to calculate the lattice heat capacities of aluminium and thorium, we divided the first Brillouin zone into an equally spaced sample of 8000 points. These 8000 points were reduced to 262 non-equivalent wave vectors due to crystal symmetry. The phonon frequencies were calculated by solving the secular determinant for all these wave vectors. The resulting phonon spectrum was used to calculate the lattice heat capacities of alumi-

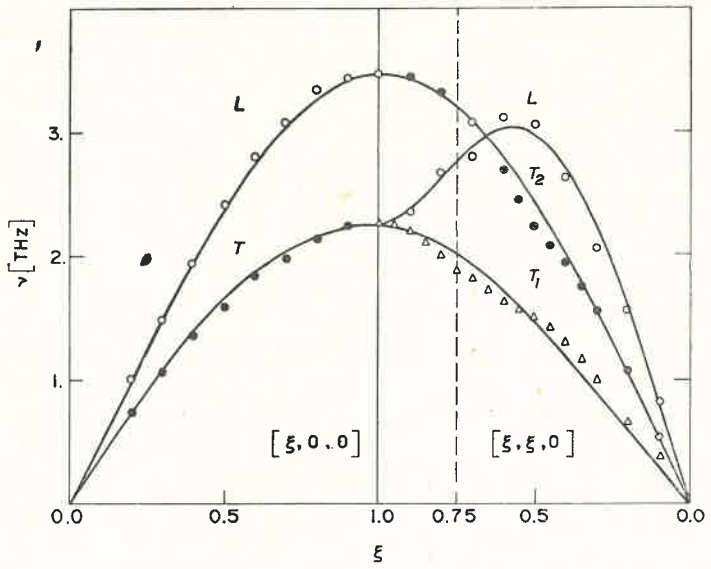

Fig. 3. Phonon dispersion relations in thorium along the $|00\xi|$ and $|\xi\xi 0|$ directions. Captions are the same as for Fig. 1

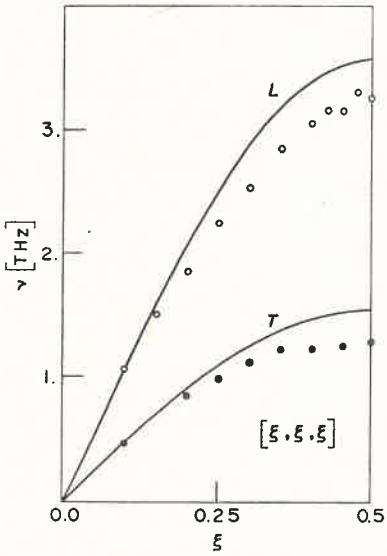

Fig. 4. Phonon dispersion relations in thorium along $|\xi\xi\xi|$ direction. Captions are the same as for Fig. 1

nium and thorium by Bleckmann's technique. The evaluation of the Debye temperature follows from a knowledge of the theoretical C_v and the temperature at which it was calculated. The calculated $(\theta - T)$ curves of aluminium and thorium are plotted in Figs 5 and 6. For aluminium the experimental $(\theta - T)$ curves is also shown in Fig. 5 by the symbol given in the caption. To estimate the C_v of the crystal, the coefficient of the electronic heat capacity γ was subtracted from the experimental C_v. The experimental C_v of alu-

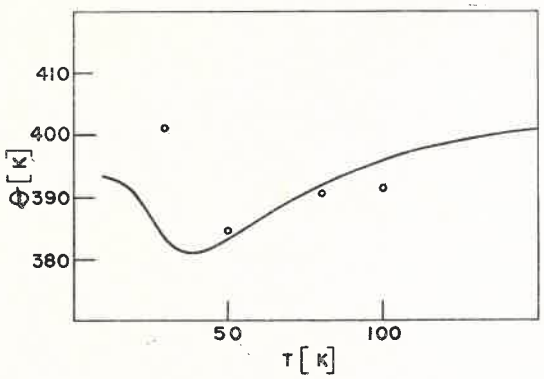

Fig. 5. (θ–T) curves for aluminium. The theoretical curve is shown by a solid line. Experimental points are shown by ○

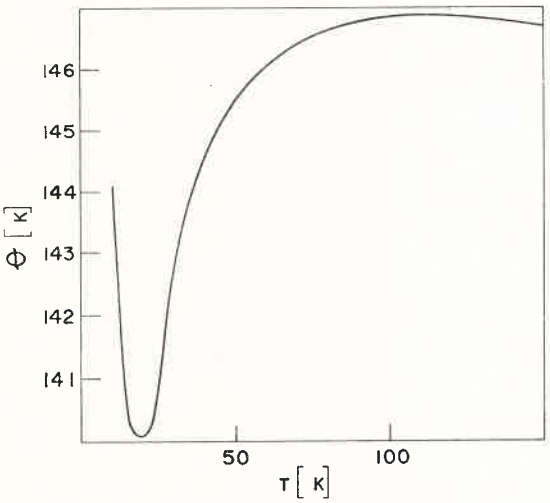

Fig. 6. (θ–T) curves for thorium

minium corresponds to the measurement of Giaugne and Meads [14] and $\gamma = 3.27 \times 10^{-4}$ cal mol^{-1} deg^{-2} corresponds to the measurement of Howlinge et al. [15]. For thorium, experimental C_v data does not exist.

4. *Discussion*

For the sake of convenience we shall discuss each metal separately.

Aluminium

A critical study of the results predicted by the present calculations reveals the following:

1. The calculated phonon dispersion curves of aluminium along the three symmetry directions, $|\xi\,00|$, $|\xi\xi\,0|$ and $|\xi\xi\xi|$, are found to be in excellent agreement with the experi-

mental results of Stedman and Nilsson [10]. The calculated curves differ from the experimental ones by a few wave vectors only, especially near the zone boundary. A small difference between the two sets of results is noticeable only in the transverse branches of all the symmetry directions. Nevertheless, maximum discrepancy found between the calculated and experimental frequencies is of the order of 6 to 7%. This kind of result is quite reasonable owing to the fact that we have not included the experimental error in plotting the curves.

2. The calculated $(\theta - T)$ curve of aluminium is found to reproduce the entire trace of the experimental curve. We have compared theoretical results with the experimental observations at a few points only. If we confine the comparison to the region between $T = 50°K$ and $100°K$, our calculated curve does not differ from the experimental one by more than 3%. A large discrepancy near $T = 30°K$ reveals either that the sampling technique was unsuitable at and below that temperature or a large error in the experimental observations exists.

3. We have found that electron screening in metallic aluminium is governed by the theory of Bohm and Pines.

Theorium

A study of results reported for thorium reveals the following:

1. The calculated phonon dispersion curves of thorium have given an excellent account of the experimental results of Reese et al. [11]. Calculated phonon frequencies are found to reproduce extremely well the experimental dispersion curves along the $[\xi\, 00]$ and $[\xi\xi\, 0]$ directions. A discrepancy of the order of 10% exists in the $|\xi\xi\xi|$ directions for the high frequency region.

2. In the absence of an experimental $(\theta - T)$ curve of this metal, we have plotted the calculated curve for the benefit of experimentalists.

3. Electron screening in this metal was also varied between the limits predicted by the theories of Bohm and Pines and that of Thomas and Fermi. It was found that best results were obtained from the theory of Bohm and Pines.

5. Conclusion

The present study of the theoretical phonon dispersion relations along the three principal symmetry directions and lattice heat capacities of aluminium and thorium by means of a phenomenological model involving only five free parameters has given a very good account of the experimental results.

Except for a few wave vector in the high frequency region for phonon propagating in all the symmetry directions. the theoretical curve has produced the experimental results within the limits of the experimental errors. To obtain similar kinds of results, the experimentalists, Stedman and Nilsson [10] for aluminium and Reese et al. [11] for thorium, have employed as many as 24 free parameters in their point ion model studies. Even though they used such a huge number of parameters in their studies they could not get results which agreed well with the experimental elastic constants, a consequence which resulted

from ignorance of the electron-ion interaction in metals. We have, on the other hand, obtained good agreement with the elastic constants and the experimental phonon frequencies.

The comparison and success of the $(\theta - T)$ curve is to a certain extend an independent check of the model.

For aluminium, enormous theoretical lattice dynamical studies exist in literature for both schemes, phenomenological and first principles. In the phenomenological study, the work of Shukla and Dayal [16] is noteworthy. In models on first principles the work of Wallace [17], Animalu et al. [18] and that of Rao [19] are worth mentioning. A comparative study of the results given by these workers with those predicted from the present studies may reveal that the present result is in no way inferior to those cited above. The success of the present study lies on two aspects; first, the consideration of the short range ion-ion interaction on axially symmetry forces which controls the slopes of the dispersion curves in the lower frequency region, and second, the use of electron-ion interaction on a very good model, Kreb's model, which has got to a certain extent an origin similar to models based on first principles.

For thorium no sophisticated model has been applied to a theoretical lattice dynamical study. The study of Cavalheiro and Shukla [20] is inferior to the present one.

Comparing the previous studies of Shukla and Colaborators with the present one, one can see that the present phenomenological model successfully reproduces the experimental lattice dynamical properties of almost all cubic metals.

As far as the electronic screening in cubic metals is concerned, we have found that for all metals the screening parameter based on the theory of Bohn and Pines gives the best results.

The Thomas-Fermi screening has been found quite unsuitable for lattice dynamical studies.

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