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L.M. Brescansin, N.T. Padial and M.M. Shukla

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The Lattice Dynamics of Six Prominent B.C.C. Transition Metals

L.M. BRESCANSIN, N.T. PADIAL AND M.M. SHUKLA

Instituto de Física "Gleb Wataghin"

Universidade Estadual de Campinas

C.P. 1170, Campinas, S.P., Brasil.

Abstract

The frequency versus wave vector dispersion relations along the three principal symmetry directions, [ξ00], [ξξ0] and [ξξξ], of six prominent body centered cubic transition metals, namely that of molybdenum, α-iron, tungsten, tantalum, niobium and that of chromium, have been computed on the basis of a phenomenological model proposed by the present authors recently. The calculated results are in very good agreements to the experimental findings.

1. INTRODUCTION

Among cubic metals the transition metals are the neglected ones as far as their theoretical lattice dynamical studies are concerned. This is due to the fact that conduction electrons in these metals do not lie in the well defined electronic states leaving behind a multiple and doubtful valency to them. Also, the ion cores of these metals are not small as demanded by the ideal metals. Both properties of these metals render them unsuitable and complicated for theoretical lattice dynamical studies on models on first principles. This is the reason why in recent past several workers[1-5] have carried out the lattice dynamical studies of these metals on the basis of phenomenological models.

There are, in all, ten transition metals of cubic structure and they are: nickel, platinum, palladium, α-iron, vanadium, molybdenum, tungsten, tantalum, niobium and chromium. Nickel, platinum and palladium belong to the f.c.c. structure and the rest seven are b.c.c. structure. The transition metals of f.c.c. structure almost follow a homology rule as far as their phonon spectra are concerned, thus their lattice dynamics is not very much complicated, as compared to metals of b.c.c. structure where the homology rule breaks down.

Recently the present authors (see Shukla et al[6]) have developed a phenomenological model for cubic metals by considering the ion-ion interactions on the basis of axially symmetric model of Lehman et al[7]. The electron-ion interaction was adopted on Krebs'[8] formalism. Our scheme has been found extremely successful in interpreting the experimental phonon dispersion relations in alkali metals (see Lima et al[9]), noble metals (Closs and Shukla[10]) and (Shukla and Closs[11] and f.c.c. transition metals (Closs and Shukla[12]). A great success of this model for several metals has tempted us to take up the lattice dynamical study of six b.c.c. transition metals on its basis. To facilitate the theoretical study, extensive experimental data for the phonon dispersion relations along the principal symmetry directions of these metals exist.

2. THEORY

The frequencies of vibration of the b.c.c. metals can be obtained from the solution of the 3 x 3 determinantal equation of the form

$$|D_{\alpha\beta}(q) - m\omega^2 I\delta_{\alpha\beta}| = 0 \qquad (1)$$

where m is the ionic mass, ω is the angular frequency, I is the unit matrix of order three. Each element of the dynamical matrix $D_{\alpha\beta}(q)$ is split up into two parts: the ion-ion interaction part, $D^{ii}_{\alpha\beta}(q)$ and the electron-ion interaction part $D^{ie}_{\alpha\beta}(q)$. Written mathematically

$$D_{\alpha\beta}(q) = D^{ii}_{\alpha\beta}(q) + D^{ie}_{\alpha\beta}(q) \tag{2}$$

By confining the ion-ion interactions up to second neighbours only we get the explicit expressions for the typical diagonal and non-diagonal parts of the dynamical matrices, given by (see Lehman et al[7] and Krebs[8])

$$D^{ii}_{\substack{\alpha\alpha \\ \alpha\to i}}(q) = 8/3\, A_1 [(1 - C_i C_j C_k) + 2A_2 (1 - C_{2i})]$$

$$+ 8\, B_1 [(1 - C_i C_j C_k) + 2\, B_2 (3 - C_{2i} - C_{2j} - C_{2k})] \tag{3}$$

$$D^{ii}_{\substack{\alpha\beta \\ \alpha\to i \\ \beta\to j}}(q) = 8/3\, A_1\, S_i S_j C_k \tag{4}$$

$$D^{ie}_{\substack{\alpha\alpha \\ \alpha\to i}}(q) = \frac{1}{4}\, a^3 \lambda^2\, Ke \sum_h \left[\frac{(q_i + h_i)^2\, g^2(u_1)}{|q+h|^2 + \frac{q^2\alpha^2}{4\pi^2} f(t_1)} - \frac{h_i^2}{h^2 + \frac{q^2\alpha^2}{4\pi^2} f(t_2)}\, g^2(u_2) \right] \tag{5}$$

$$D^{ie}_{\substack{\alpha\beta \\ \alpha\to i \\ \beta\to j}}(q) = \frac{1}{4}\, a^3 \lambda^2\, Ke \sum_h \left[\frac{(q_i + h_i)(q_j + h_j)\, g^2(u_1)}{|q+h|^2 + \frac{a^2\lambda^2}{4\pi^2} f(t_1)} - \frac{h_i h_j}{h^2 + \frac{a^2\lambda^2}{4\pi^2} f(t_2)}\, g^2(u_2) \right] \tag{6}$$

In the above expressions (A_i, B_i) are the axially symmetric force constants for the i th neighbour.

$$S_i = \sin(\pi a K_i) \quad C_i = \cos(\pi a K_i), \quad q_i = \frac{aK_i}{2\pi}$$

$$\lambda = C\left(\frac{r_s}{a_0}\right)^{1/2} K_F \text{ with } 353 \leq C \leq 814$$

$$g(u) = 3(\sin u - u \cos u)/u^3 \tag{7}$$

$$f(t) = \frac{1}{2} + \frac{1 - t^2}{4t} \ln \frac{1 + t}{1 - t} \tag{8}$$

$$t_1 = \pi \ |q + h| / aK_F \tag{9}$$

$$t_2 = \pi h / aK_F \tag{10}$$

$$u_1 = 2\pi \frac{r_s}{a} \ |q + h| \tag{11}$$

$$u_2 = 2 \frac{r_s}{a} \ h \tag{12}$$

(K_i, h_i) are the cartesian components of the direct and reciprocal wave vectors. K_F is the Fermi wave vector r_s is the radius of atomic sphere, a_o is the Bohr radius and Ke is the Bulk modulus of the electron gas.

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

$$a C_{11} = 2/3 A_1 + 2A_2 + 2B_1 + 2B_2 + aK_e \tag{13}$$

$$a C_{12} = A_1 - 2B_1 - 2B_2 + aK_e \tag{14}$$

$$a C_{44} = 2/3 A_1 + 2B_1 + 2B_2 \tag{15}$$

$$a K_e = C_{11} - C_{12} + 4/a (B_1 + B_2) \tag{16}$$

3. PHONON DISPERSION RELATIONS ALONG THE SYMMETRY DIRECTIONS

Along symmetry directions the secular determinant factorizes and the following simple algebraic relations are obtained to calculate the phonon frequencies:

$$m\omega^2 L\,(00\xi) = 8 \frac{A_1}{3} + B_1 \,|1 - C_i| + D_{ii}^{ie} \tag{17}$$

$$m\omega^2 L\,(00\xi) = 8 \frac{A_1}{3} + B_1 \,|1 - C_i| + D_{kk}^{ie} \tag{18}$$

$$m\omega^2 L\,(0\xi\xi) = 8\frac{2A_1}{3} + B_1 \,|1 - C_i^2| + 2(A_2 + B_2) \,|1 - C_{2i}| + D_{ii}^{ie} + D_{ij}^{ie} \tag{19}$$

$$m\omega^2 T_1\,(0\xi\xi) = 8 B_1 \,|1 - C_i^2| + 2(A_2 + B_2) \,|1 - C_{2i}| + D_{ii}^{ie} + D_{ij}^{ie} \tag{20}$$

$$m\omega^2 T_2(0\xi\xi) = 8\left(\frac{A_1}{3} + B_1\right)[1 - C_i^2] + 2(A_2 + 2B_2)[1 - C_{2i}] + D_{kk}^{ie} \qquad (21)$$

$$m\omega^2 T(\xi\xi\xi) = 8/3\, A_1[1 + 2C_i - 3C_i^3] + 8B_1[1 - C_1^3] + 2(A_2 + 3B_2)[1 - C_{2i}] + D_{ii}^{ie} + 2D_{ii}^{ie} \qquad (22)$$

$$m\omega^2 T(\xi\xi\xi) = 8/3\, A_1[1 - C_i] + 8B_1[1 - C_i^3] + 2(A_2 + 3B_2)[1 - C_{2i}] + D_{ii}^{ie} - D_{ij}^{ie} \qquad (23)$$

4. NUMERICAL COMPUTATIONS

The five disposable parameters, A_1, A_2, B_1, B_2 and aK_e of the model were determined with the help of five independent equations, three relating the atomic force constants with elastic constants and two with phonon frequencies of the zone boundaries. We made several choices of these two frequencies and found that longitudinal zone boundary from [00ξ] direction and transversal from [ξξξ] gave the best fit with the experimental data. As the experimental phonon frequencies of all the six metals were determined at room temperature only, the room temperature values of the elastic constants were used in the calculation of the atomic force constants. The input data, the elastic constants for α-iron[14], molybdenum[18], tungsten[16], tanntalum[15], niobium[17] and chromium[13] and the zone boundaries frequencies[19-25] of all the six metals are shown in Table 1. The output values of the force constants are given in Table 2. The computed phonon dispersion curves of all the six metals are shown in figures 1 to 6 together with experimental phonons, also shown for comparison purposes. While the calculated curves are shown by solid lines, the experimental points are plotted as marked by the different symbols given in the captions.

5. DISCUSSION AND CONCLUSION

A critical study of figures 1 to 6 reveals that the calculated phonon dispersion relations for all the six metals along all the three principal symmetry directions have given an excellent description of the experimental results. For four metals, namely α-iron, molybdenum, tungsten and chromium the calculated results are found in better agreements with the experimental results

compared to tantalum and niobium.

The calculated phonons at the low wave vectors have almost reproduced the experimental results within the limits of the experimental results. A little discrepancy has been found between the calculated and experimental phonons in the high frequency ends, near the zone boundaries. The maximum deviations found between the calculated and experimental phonons do not exceed more than 10%. This kind of result is not very much surprising owing to the fact that we have completely ignored the experimental errors in the calculations of the force constants as well as in the plot of the experimental results. A careful look in the literature may reveal that experimentalists ie. Shaw and Muhlestein[17] for chromium, Brockhouse et al[20] for α-iron, Woods[21] for tantalum, Chen et al[22] for tungsten, Nakagawa and Woods[23] for niobium and Woods et al[24] for molybdenum, had to employ as many as 12 to 26 free parameters in their point ion model fit of the dispersion curves. Even the use of such a great number of parameters has not served the purpose as they could not fit very well the low frequency regions of the experimental phonons.

The other existing theoretical studies of the lattice dynamics of b.c.c. transition metals on phenomenological model[1-5] are found to be quite inferior to the present results. In that context we should mention here only the work of Lahteenkorva[2] and that of Bajpai and Neelakandan[1] as these authors have also employed axially symmetric forces to represent the ion-ion interaction. The work of Lahteenkorva[2] is found to be quite inferior in the $[\xi\xi 0]$ direction for niobium, tantalum and tungsten compared to present results. This is due to the reason that he has completely ignored complety the electron-ion interaction in metals. The result of Bajpai and Neelakandan[1] is also found to be inferior to the present calculations noticeable differences can be found for the metals tantalum and tungsten especially in the $[\xi\xi\xi]$ directions. This kind of result is quite expected as Bajpai and Neelakandan[1] have used the electron-ion interaction in metals on the basis of the model of Sharma and Joshi[23] which has got severe limitations. The present result, thus, presents a reasonable account of the experimental results in six prominent b.c.c. transition metals on the basis of a phenomenological model which has been found quite successful in the study of almost all cubic metals.

We would like to mention that experimental phonon dispersion relations in several b.c.c. transitions metals exhbibit peculiar features. Some remarkable features of niobium and tantalum are (Woods[24]);

(1) The extra maximum and minimum in longitudinal branch of $[\xi\xi\xi]$;

(2) Te crossing of longitudinal and transverse branch of $[\xi 00]$ near $\xi = 7$;

(3) The crossing of two transverse branches in $[\xi\xi 0]$ direction;

(4) The untrsual shape of longitudinal branch of $[\xi 00]$ near $\xi = 46$.

The explanation of these experimental observations are beyond the capecity of the phenomenological models.

Our model is very crude model in a sense that it can not control properly the complex

nature of the electron-ion interactions in these metals. Some of the experimental results have been explained reasonably well in the recent work of Animalu[25] using pseudopotential technique.

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CAPTIONS FOR FIGURES

Fig. 1 - Phonon dispersion relations in α-iron along the $|\xi 00|$, $|\xi\xi 0|$, and $|\xi\xi\xi|$ directions. Solid lines show the computed results. Experimental points are shown by o, ● and Δ.

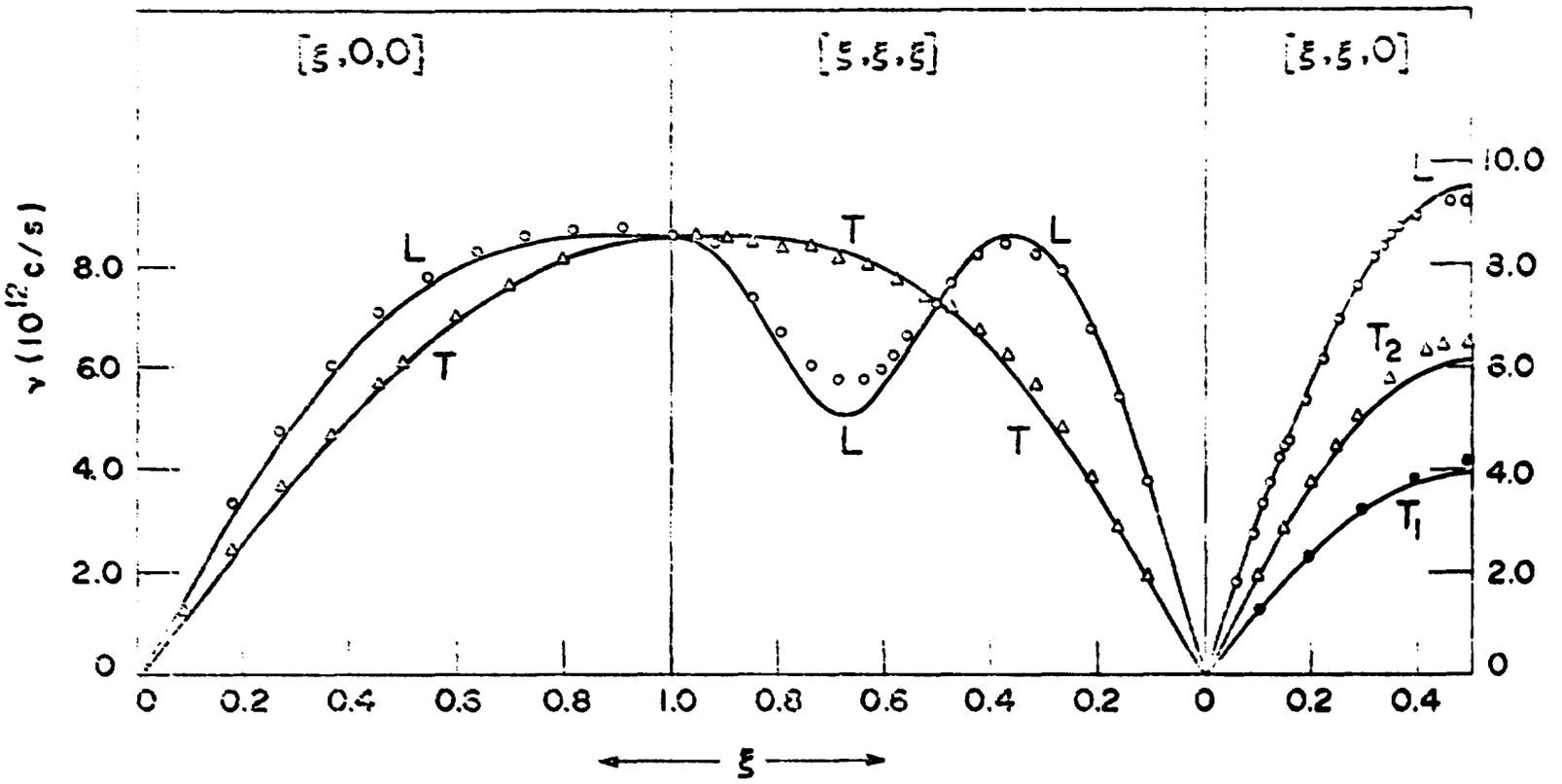
Fig. 2 - Phonon dispersion relations in Molybdenum. Captions are the same as for figure 1.

Fig. 3 - Phonon dispersion relations in tungsten. Captions are the same as for figure 1.

Fig. 4 - Phonon dispersion relations in niobium. Captions are the same as for figure 1.

Fig. 5 - Phonon dispersion relations in tantalum. Captions are the same as for figure 1.

Fig. 6 - Phonon dispersion relations in chromium. Captions are the same as for figure 1.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[ξ,ξ,0]
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T
L
T
L
T
L
T
T2
T1
0
2.0
4.0
6.0
8.0
10.0
0
0.2
0.4
0.6
0.8
1.0
0.8
0.6
0.4
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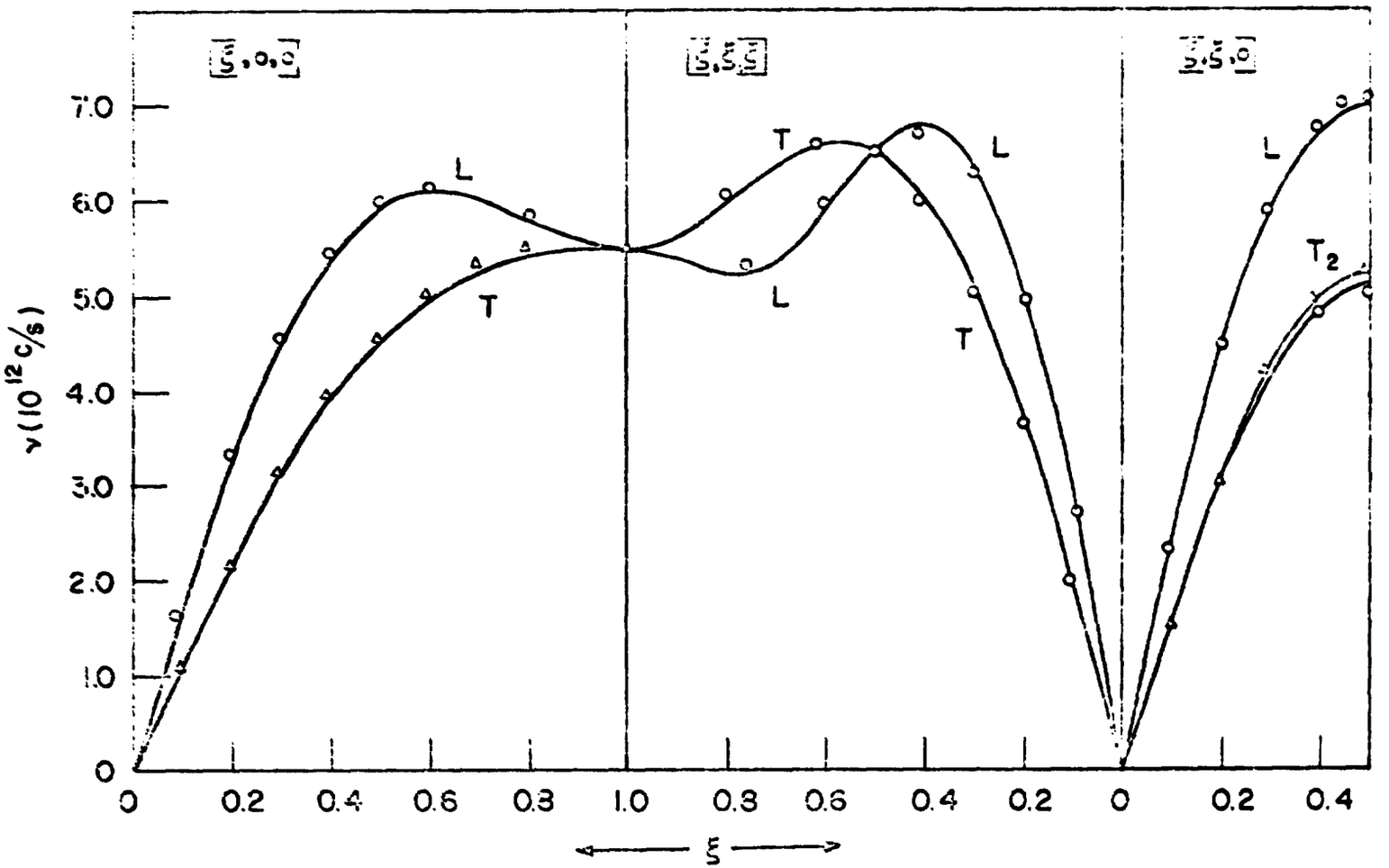
0
0.2
0.4
ξ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[ξ,ξ,ξ]
[ξ,ξ,0]
L
T
L
T
L
T
L
T
T2
ν(10^12 c/s)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0
0.2
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1.0
0.8
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0.4
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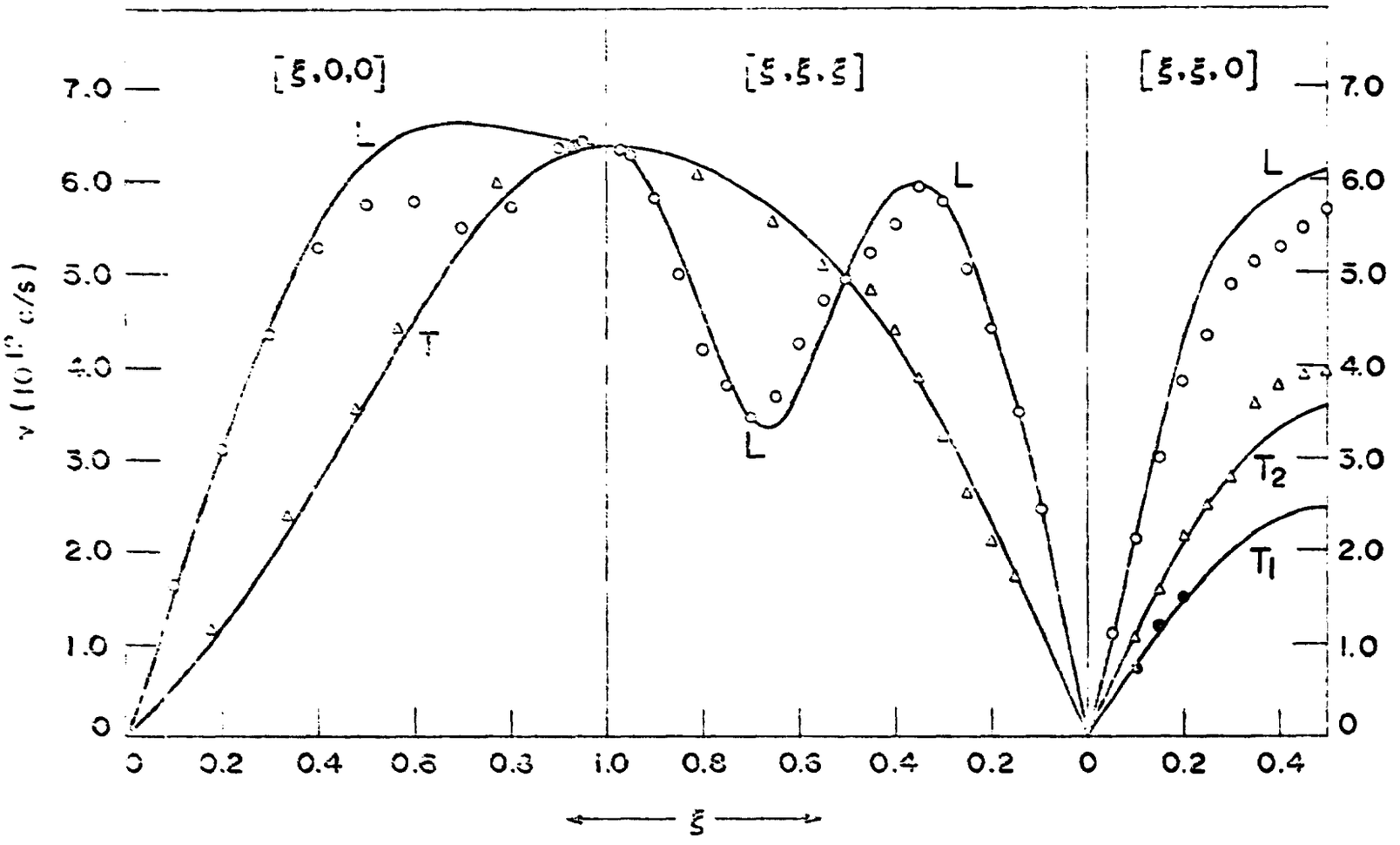
0
0.2
0.4
ξ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[ξ,ξ,0]
L
T
L
L
T2
T1
ν (10^12 c/s)
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6.0
5.0
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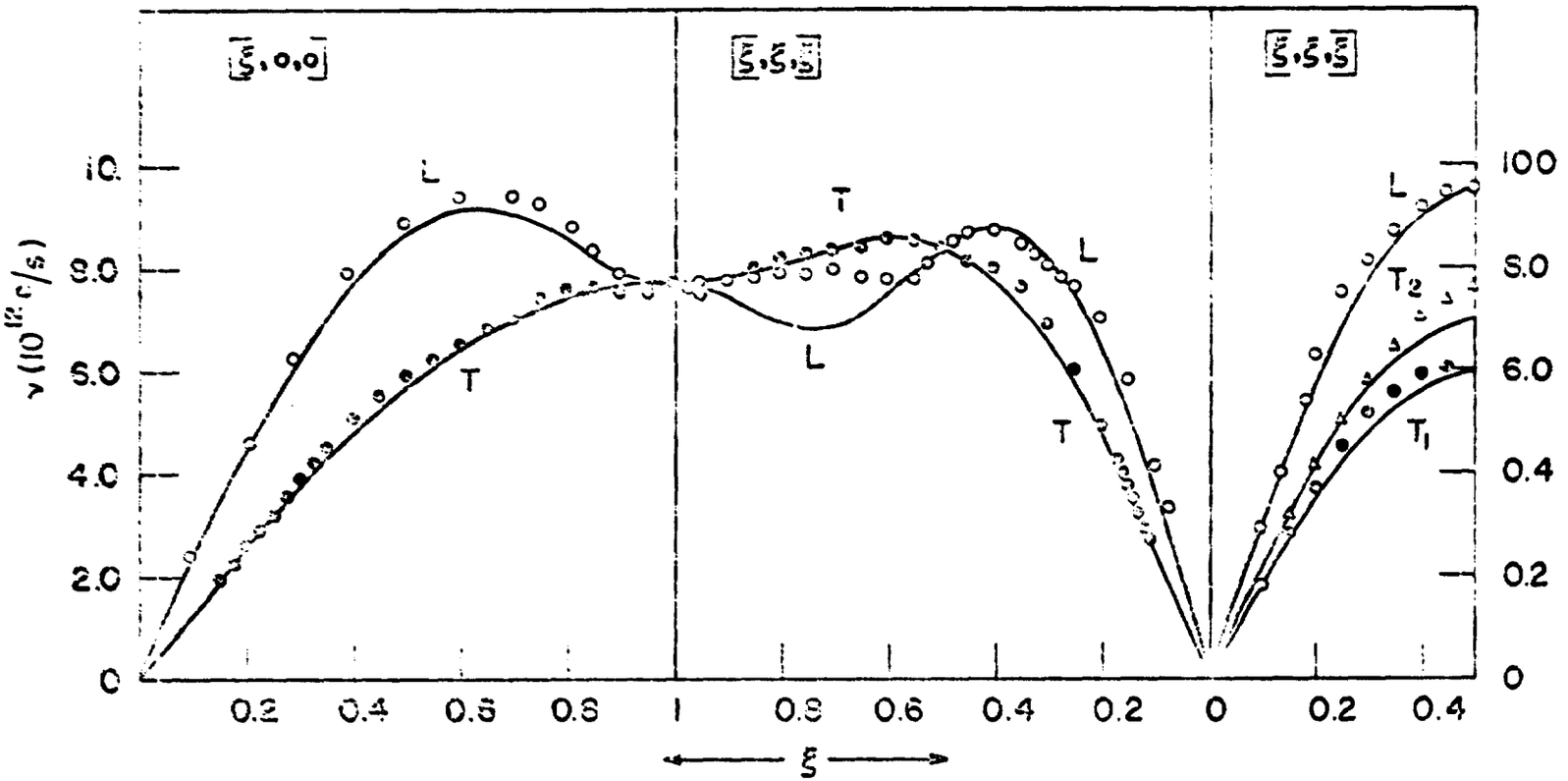
ξ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[ξ,ξ,ξ]
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2.0
0
100
8.0
6.0
0.4
0.2
0
L
T
L
T
L
T
L
T
T2
T1
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0.6
0.8
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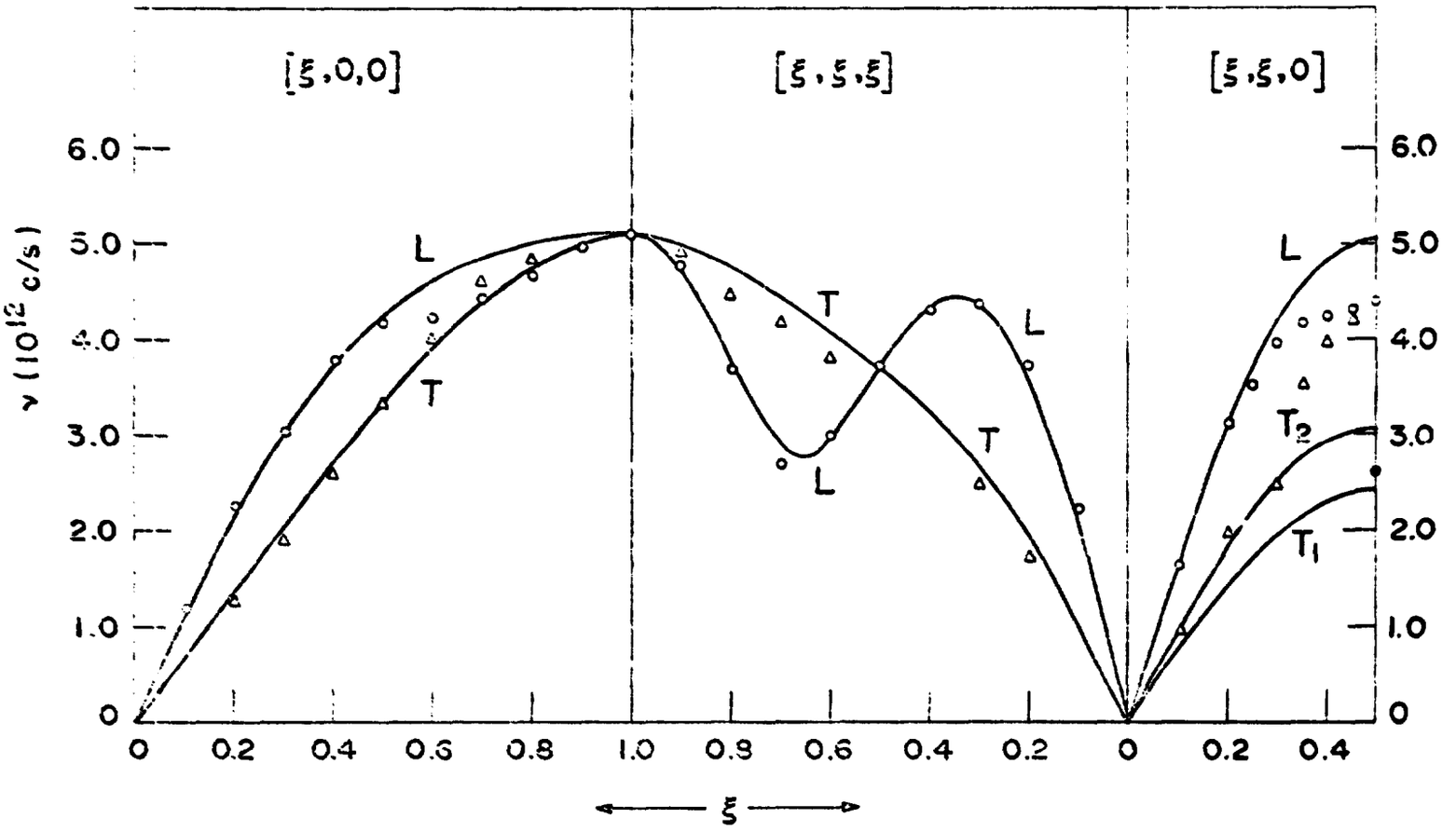
0.4
ξ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L
T
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T
L
T
L
T
T2
T1
0
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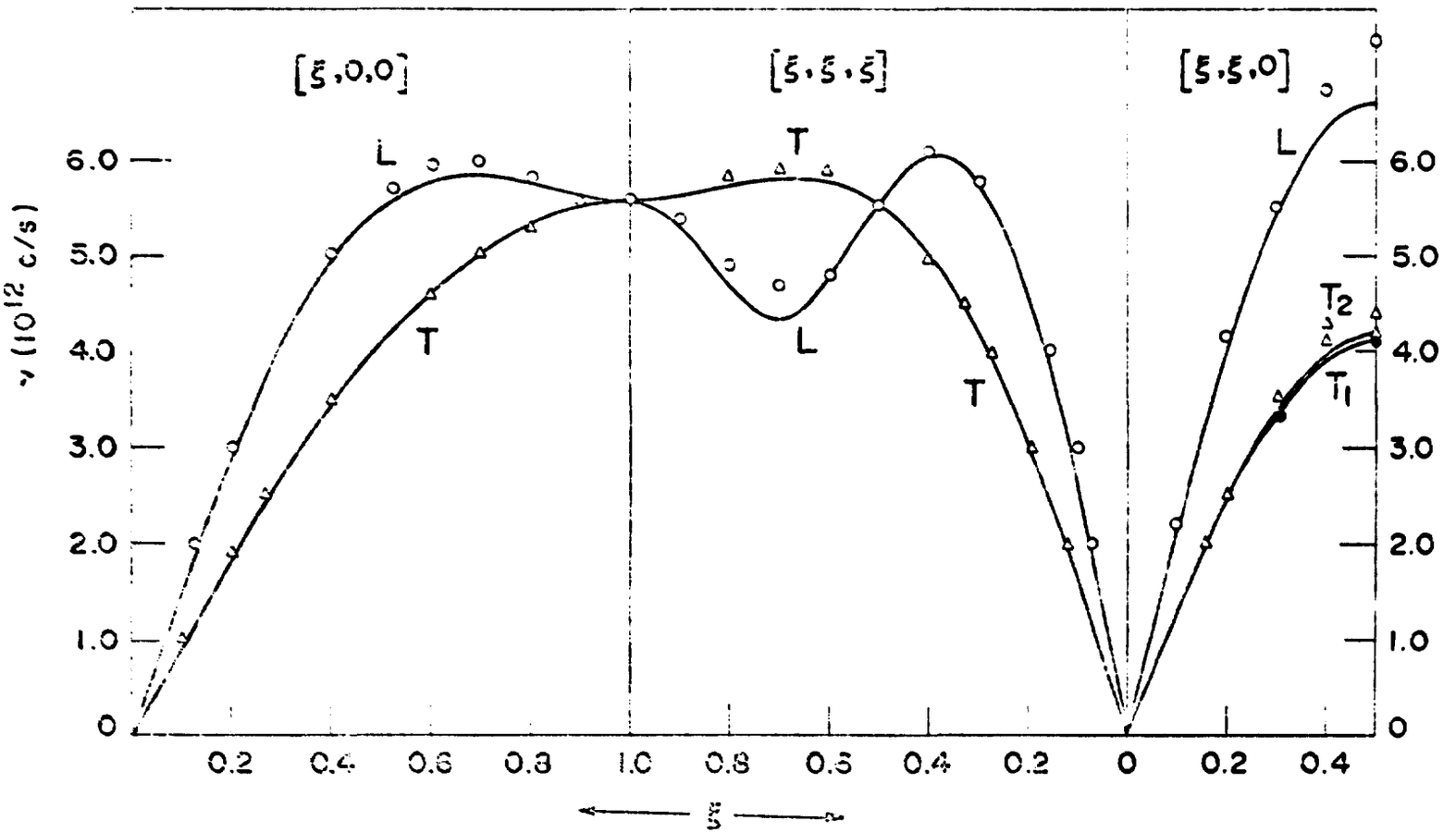
ξ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L
T2
T1
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5.0
4.0
3.0
2.0
1.0
0
ν (10^12 c/s)
0.2
0.4
0.6
0.8
1.0
0.8
0.6
0.4
0.2
0
0.2
0.4
ξ

TABLE 1

INPUT DATA TO CALCULATE ATOMIC FORCE CONSTANTS

METALS	ELASTIC CONSTANTS C_{11}	C_{12}	C_{44}	LATTICE PARAMETER	ATOMIC MASS	PHONON FREQUENCIES THZ	
	10^{12} dyn cm^{-1}			A°	$10^{-23}g$	νL (ξξξ)	νT (00ξ)
Chromium	3.50[13]	6.78[13]	10.10[13]	2.884	8.631	7.66[17]	8.38[17]
α-iron	2.331[14]	1.354[14]	1.178[14]	2.866	9.270	8.52[18]	7.28[18]
Tantalum	2.609[15]	1.574[15]	.818[15]	3.306	3.001	5.03[19]	3.78[19]
Tungsten	5.233[15]	2.045[15]	1.607[15]	3.165	3.053	5.50[20]	5.50[20]
Niobium	2.465[16]	1.345[16]	.287[16]	3.301	1.542	6.49[21]	5.04[21]
Molybdenum	4.408[15]	1.724[15]	1.217[15]	3.147	1.592	5.51[22]	6.53[22]

TABLE 2

OUT PUT VALUES OF THE FORCE CONSTANTS
UNIT OF 10^{3} dyn cm^{-1}

METALS	α	β	γ_1	γ_2	aKe
Chromium	24.631	28.043	4.228	2.097	15.783
α-iron	50.682	14.029	-.380	.372	50.111
Tantalum	42.937	18.684	4.029	4.815	21.842
Tungsten	51.253	33.765	4.857	3.489	47.253
Niobium	45.441	39.301	5.070	10.912	-6.708
Molybdenum	22.184	18.732	3.753	7.995	32.979