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MODIFIED TENSOR FORCE MODEL FOR LATTICE DYNAMICS OF BODY CENTERED CUBIC TRANSITION METALS*

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The phonon dispersion relations along the three principal symmetry directions i.e. $[00\xi]$, $[\xi\xi 0]$ and $[\xi\xi\xi]$, and $(\theta - T)$ curves of α-iron, molybdenum, chromium and tungsten are computed on a modified tensor force model recently proposed by us. The computed results are in fair agreement with the experimental observations.

1. *Introduction*

Quite recently Bonelli and Shukla [1] and [2], (hereafter referred to as I and II) proposed a modified tensor force model (MTFM) for the study of the tallice dynamics of b.c.c. metals. Our earlier studies (I and II) on sodium, potassium, lithium and rubidium have shown that MTFM has reproduced remarkably well the experimental results for the entire phonon dispersion relations along the principal symmetry directions as well as the lattice heat capacities of these metals. The fact that alkali metals are monovalent with very small values of elastic constants is responsible for the negligible influence of the electron-ion interaction part of the dynamical matrix over the computed phonons. That is why the success of the model for monovalent alkali metals was not surprising.

We, thus, took to the task of testing MTFM for some metals. We chose for the present study the four b.c.c. transition metals i.e. α-iron, molybdenum, chromium and tungsten.

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We knew for sure that these metals are quite complicated due to the reason that they do not have a definite number of conduction electrons per unit volume as required to fit in to our model. We could choose a variety of values such as an integer (from 2 to 6) on a fraction (2, 6, 2, 3 etc.) as the conduction electrons of these metals lie in hybrid (*spd*) states. Also we knew that the experimental elastic constants of these metals were large compared to alkali metals. Which thus shows that the electrcn-ion interaction part of the dynamical matrix will have pronounced influence on the computed phonons. Confronted with these two difficulties, we present in this paper the theoretical phonon dispersion relations along the principal symmetry directions and the variation of Debye temperature with temperature of these metals. To facilitate our theoretical studies reliable experimental data are available for comparison purpose.

2. *Numerical computations*

We have followed our previous work (I) as far as the evaluation of the model parameters, computation of phonon dispersion relations along the principal symmetry directions and the $(\theta - T)$ curves for a metal is concerned. The five disposable parameters of the model were determined with help of five independent experimental constants, namely three elastic constants and two phonon frequencies from the boundary of the Brillouin zone. The input data to calculate the model parameters are given in Table I. The output

TABLE I

Input data used in calculation

Substrate	Elastic constants [reference] Unit 10^{12} dyn cm^{-2}	Atomic mass [reference] Unit 10-23 gr	Lattice constants [reference] Unit 10^{-8} cm	Zone boundary Frequency [reference] Unit 10^{12} Hz
α-ion	$C_{11} = 23.30$ $C_{12} = 13.54$ [3] $C_{44} = 11.78$	9.271 [6]	2.866 [6]	$\nu_{L\xi oo} = 8.52$ [7] $\nu_{L\xi\xi\xi} = 7.28$
Molybdenum	$C_{11} = 44.08$ $C_{12} = 17.24$ [4] $C_{44} = 12.16$	15.926 [6]	3.147 [6]	$\nu_{L\xi oo} = 6.30$ [8] $\nu_{L\xi\xi\xi} = 6.53$
Chromium	$C_{11} = 35.00$ $C_{12} = 6.78$ [5] $C_{44} = 10.10$	8.631 [6]	2.884 [6]	$\nu_{L\xi\xi oo} = 7.90$ [9] $\nu_{L\xi\xi\xi} = 8.50$
Tungsten	$C_{11} = 52.33$ $C_{12} = 20.45$ [4] $C_{44} = 16.07$	30.519 [6]	3.165 [6]	$\nu_{L\xi oo} = 5.50$ [10] $\nu_{L\xi\xi\xi} = 5.50$

TABLE II

Output values of force constants in units of 10^3 dyn cm^1

Substance	α_1^1	β_1^1	α_1^2	α_2^2	aKe
α-ion	16.475	17.028	14.246	413	4.487
Molybdenum	14.505	7.426	23.431	4.638	62.849
Chromium	13.103	9.238	31.501	1.461	11.727
Tungsten	21.028	14.978	33.392	4.403	55.678

values of the force constants are given in Table II. The computed phonon dispersion relations along three principal symmetry directions, namely [00ξ], [ξξ0] and [ξξξ] of α-iron, molybdenum, chromium and tungsten are shown respectively in figures 1 to 4. Also shown in these figures are the experimental phonons for comparison purpose. In figures 5 to 8 the computed and experimental $(\theta - T)$ curves of α-iron, molybdenum, chromium and tungsten are shown. We have taken care to deduct the electronic part of C_v, i.e. γT from the experimental C_v to derive the lattice part. The experimental

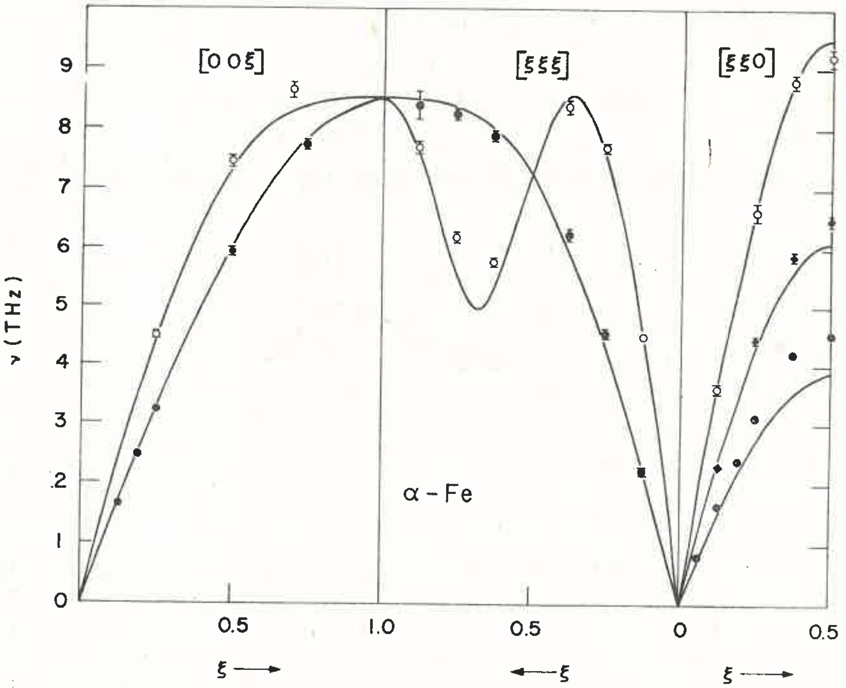

Fig. 1. Phonon dispersion relations in α-iron along the symmetry directions [00ξ], [ξξξ] and [ξξ0]. ξ is the reduced vector. Theoretical curves are shown by continuous lines. Experimental points are shown by the different symbols used in the figure

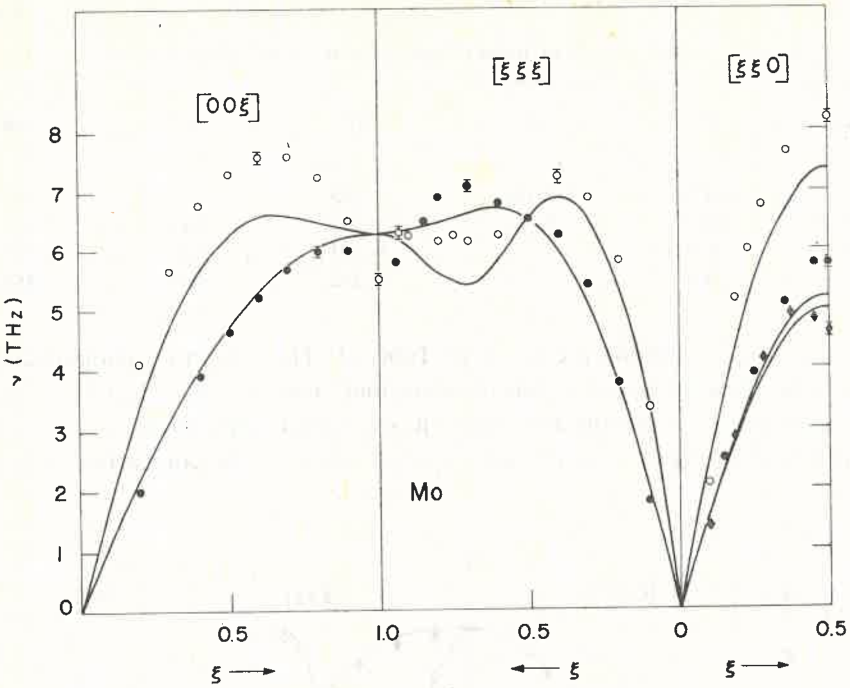

Fig. 2. Phonon dispersion relations in molybdenum. Captions are the same as for figure 1

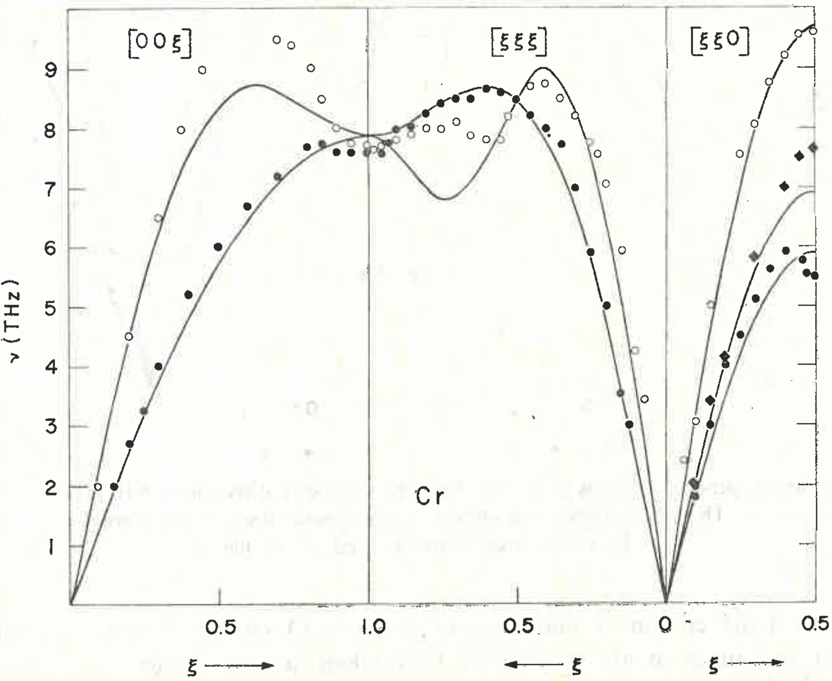

Fig. 3. Phonon dispersion relations in chromium. Captions are the same as for figure 1

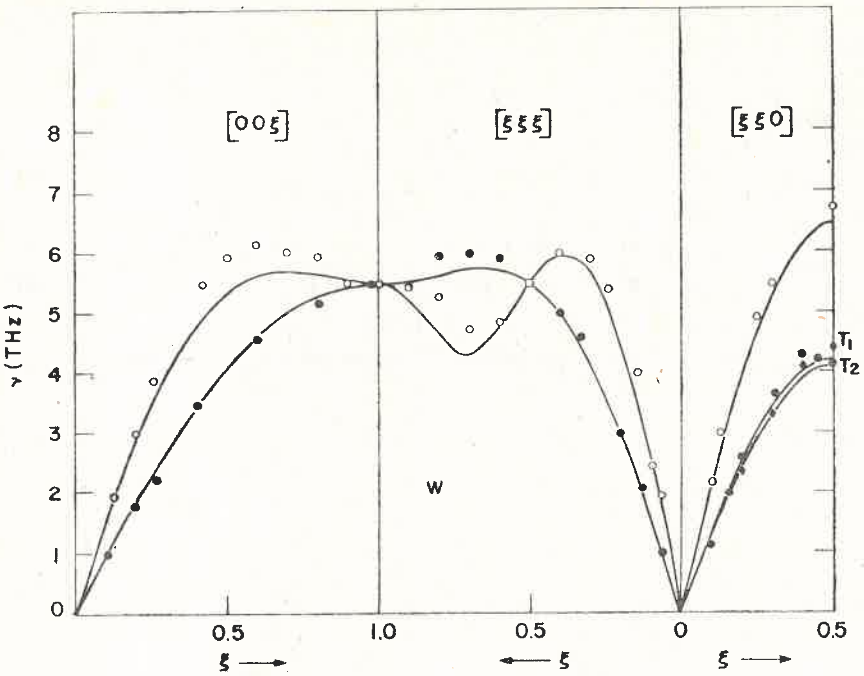

Fig. 4. Phonon dispersion relations in tungsten. Captions are the same as for figure 1

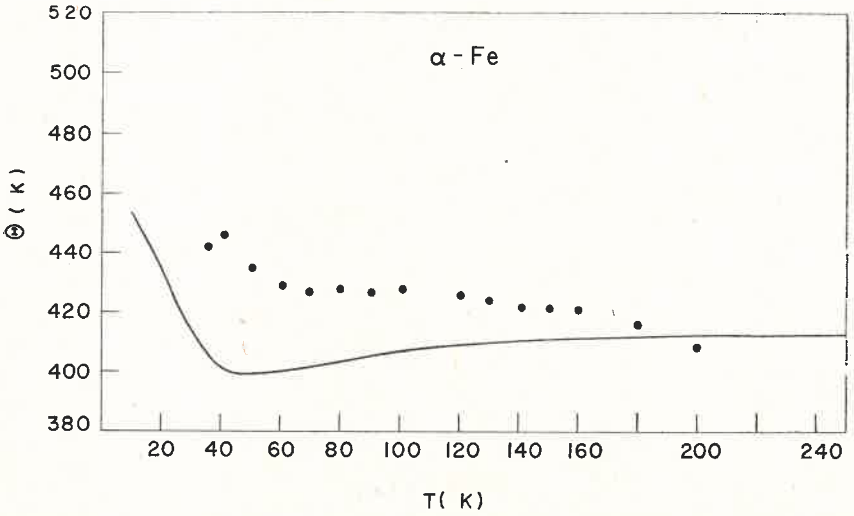

Fig. 5. $(\theta - T)$ curves of α-iron. Solid line is the computed result. Experimental values shown as points

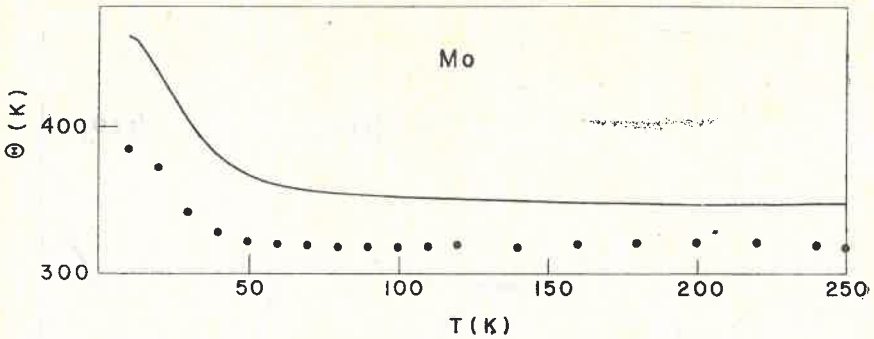

Fig. 6. $(\theta-T)$ curves of molybdenum. Captions are the same as for figure 5

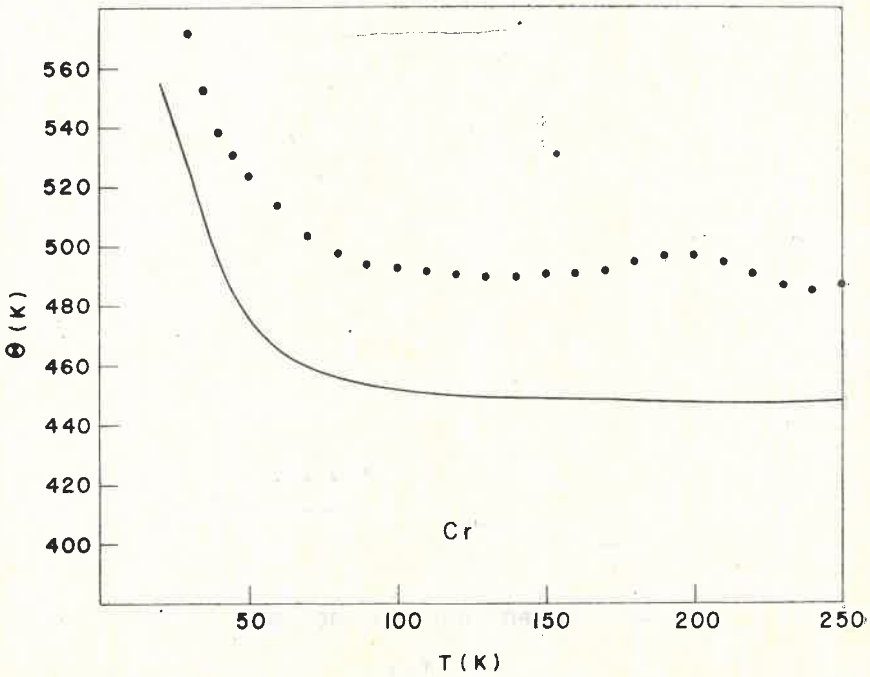

Fig. 7. $(\theta-T)$ curves of chromium. Captions are the same as for figure 5

values of C_v and γ for the metals α-iron, molybdenum, and tungsten were taken respectively from the works of Kelly [11], Clussius and Frenzosini [12] and Clussius and Frenzosini [13].

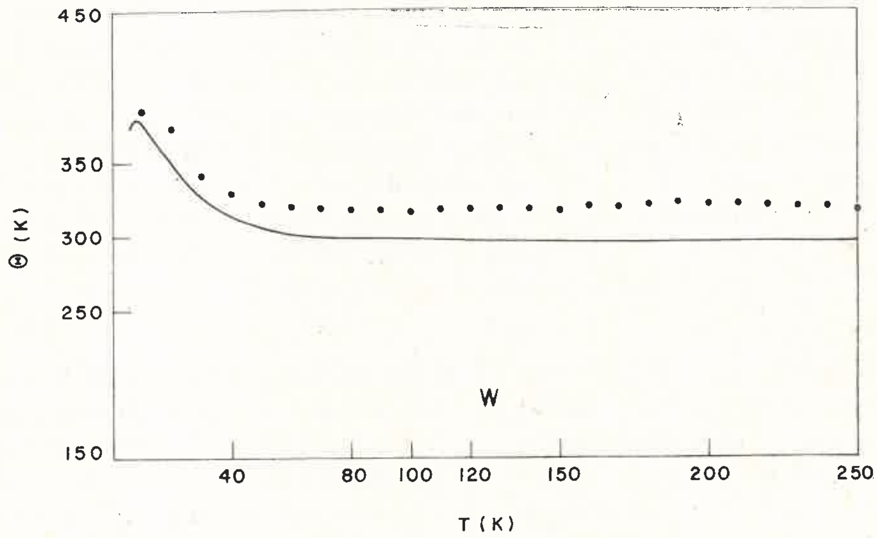

Fig. 8. $(\theta - T)$ curves of tungsten. Captions are the same as for figure 5

3. Comparison with experimental results

The computed and experimental results for each metal are compared separately. An α-iron inspection of figure 1 shows that there is excellent agreement between the computed and experimental phonons along the [ξ00] direction. Except for wave vectors near $\xi = 0.7$ the maximum departure obtained between the computed and experimental phonons is found to be 5%. For [ξξ0] direction, the transversal frequencies are found to reproduce the experimental ones within the limit of the experimental error. For the longitudinal branch the maximum departure found between the experimental and theoretical frequencies are of the order 9%. For the [ξξξ] direction the computed phonons were found to give a fair description of the transverse branch deviating by a maximum of 17% with the experimental observation.

Fig. 5 shows that the computed $(\theta - T)$ curve of α-iron has given a fair description of the experimental curve. The maximum discrepancy found between the observed and calculated θ is of the order of 10%.

Chromium

A study of figure 2 shows that there is good agreement between the computed and experimental phonons along all the three principal symmetry directions.

The computed phonons are found to depart by a maximum of 10% in the [ξ00] and [ξξξ] direction and by 9% in the [ξ00] direction. There are certain observations to be made as far as the experimental phonons are concerned. The experimental workers, Shen and Muhlenstein [9], have not determined the experimental error in the frequencies but they have pointed out that such an error would be of the order of 2%.

There are four Kohn anomalies present in the experimental phonon dispersion curves and of these two are near $\xi = 0.5$ of the longitudinal, and transverse branch of [ξξξ] and two near [ξ00]. The effect of Kohn anomalies on the experimental phonons are observed by means of a drastic dip of the experimental phonon dispersion curves at that wave vector. Our computed results are not able to demonstrate this kind of anomaly.

A study of figure 6 shows that the computed $(\theta - T)$ curve has reproduced the entire course of the experimental curve. The computed curve has always been found to lie within the experimental one. The minimum and maximum departures found between the computed and experimental curves are of the order of 9% and 20% respectively.

Molybdenum

The study of figure 3 gives information that there is good agreement between the computed and experimental phonons along all three principal symmetry directions. For this metal also, like chromium, the experimental workers, Chen and Brockhouse [9], have not measured the experimental errors corresponding to all wave vectors. As a matter of fact only for very few points of the Brillouin zone are such measurements available. We, thus, could not compare our results within the limits of the experimental errors. This metal has also got a Fermi surface similar to the metal chromium. This means that we would have four Kohn anomalies near the same vectors just as for chromium. As a matter of fact, the frequencies drop very much near $\xi = 1.0$ in the directions [ξ00] and [ξξξ]. The maximum deviation observed in the computed and experimental phonon being 13% in the longitudinal branch of [ξ00]. For the direction [ξξξ] the maximum deviation between the computed and experimental phonons is of the order of 11%. In the direction [ξξ0] such departure does not exceed more than 8% the maximum being near $\xi = 0.5$.

A study of figure 7 reveals that the computed $(\theta - T)$ curve has reproduced the entire course of the experimental curve. The computed curve lies above the experimental one. The computed θ are found to show better agreement at higher temperatures. The minimum and maximum deviation found between the calculated and experimental θ is of the order of 9% and 20% respectively.

Tungsten

A study of figure 4 shows that there is very good agreement between the computed and experimental phonons along all the symmetry directions. There is an unusual behaviour found in the experimental curve along the [ξ00] direction and that is the crossing of the longitudinal and transversal curve near the zone boundary. We did not give importance to this fact as this would not be explained on our model. Let us also remember that the experimental phonons have many uncertainties in the longitudinal branches together with the fact no measurement of the uncertainties of each phonon is available. Keeping all the above considerations for the experimental phonons we have found that our theoretical frequencies differ by 10% in all the three symmetry directions and that too in the longitudinal branches. In the transverse branches the maximum deviation found between the computed and experimental phonons (except for $\xi < 0.5$ in the $[\xi\xi\xi]$ are of the order of 5%.

A study of figure 8 shows that there is an excellent agreement between the computed and experimental $(\theta - T)$ curve for tungsten. On the whole the experimental curve is found to be above the theoretical one. The computed curve departs from the experimental one in the range of 4 to 8% only.

4. *Discussion and conclusion*

In the foregoing pages we have presented the theoretical study of the phonon dispersion relations along the three principal symmetry directions as well as the Debye temperature versus temperature curves of four b.c.c. transition metals, namely α-iron, chromium, molybdenum and tungsten. In spite of the fact that these transition metals were not simple metals for the theoretical studies on MTFM we have been able to demonstrate reasonable agreement between the computed and experimental results for all of them equally well. On the average the maximum deviation found between the calculated and experimental results were of the order of 10% for phonon frequencies and 12% for Debye temperature. We have not been able to demonstrate the observed Kohn anomalies in chromium and molybdenum.

We would like to point out that we were afraid that the large value of the bulk modulus of the electron gas would have a pronounced influence on the computed phonons in the sense that for metals having the largest value of the bulk modulus of electron gas the reproduction of the experimental results would be worst. After the computation of the entire phonon spectrum we came to the conclusion that our conjucture was baseless. One should also remember that the metals studied here are very typical ones. As regards chromium it is a metal of cubic structure which has $C_{44} > C_{12}$. Tungsten is a metal which has the isotropy factor $\frac{C_{11} - C_{12}}{2C_{44}} \approx 1$. A look at Table I would show that the computed value of the bulk modulus of the electron gas is largest for molybdenum and tungsten. Even with such a large value of computed bulk modulus (aKe), tungsten gave the best reproduction of the experimental results. This could probably reflect that the isotropy of metallic structure has been dominating. Owing to the simplicity of the model, we have no way of explaining the Koln anomaly in these metals as well as the dip in the experimental $(\theta - T)$ curve of chromium near 220 K. We have accepted all four metals as divalent. Varying valency would have little effect on the computed phonons. The use of a different kind of dielectric function (Olivero et al. [14]) would not give better results, that is why it was not tried. There are dozens of papers (see Padial et al. [15]) dealing with theoretical studies of these metals on different models. Results obtained by the present study is in no way inferior to them. We can conclude from the present study of the four b.c.c. transition metals that MTFM is a good model of b.c.c. metal.

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