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A Simple Shell Model Approach to Lattice Dynamics of Cr, Mo, and W

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Abstract

The lattice dynamics of Cr, Mo, and W are formulated in terms of a simple shell model in which the transition metal ions in the crystals are treated as deformable ions. The model involves a total of seven parameters; two charge parameters and five force constant parameters. The numerical values of the model parameters are determined by fitting to three elastic constants and the lattice vibrational frequencies measured by the neutron inelastic scattering experiments. Attempts are made to compute the phonon dispersion relations, the frequency distribution functions, and the lattice specific heats of three metals. The results are compared with experiments. It is found that the simple shell model can give a satisfactory account for the lattice vibrational characteristics of transition metals. The usefulness of the model is then discussed in comparison with other lattice dynamical models.

요 약

천이금속을 구성하고 있는 성분 이온을 변형가능한 이온으로 취급함으로써 크로미움, 몰리브데늄 및 텅스텐의 격자진동을 전자각 모델에 의해 수식화했다. 이 모델은 전하에 대한 두 변수와 다섯 개의 힘상수를 모두 합쳐 7개의 모델상수를 포함하고 있으며 이들의 수치는 금속의 탄성 계수에 관한 자료와 중성자 산란 실험에 의해 측정된 격자진동의 특성 주파수 값과 일치하도록 하여 결정했다.

한편 전자각 모델은 Cr, Mo 및 W 등 세 금속의 성파 확산곡선, 주파수 분포함수 및 비열을 계산하는데 응용하였고 그 결과를 실험치와 비교하였다. 이로부터 전자각 모델로도 천이금속의 격자진동에 대한 특성을 만족스럽게 설명할 수 있다는 것을 알아내었다. 또한 다른 격자 모델과의 비교를 통하여 전자각 모델의 유용성을 검토했다.

1. Introduction

It is characteristic of transition metals that the free ions of these metals possess the incompletely filled d-shell electrons[1]. Many band structure calculations show that the d electrons are less tightly bound to their ion core than other closed shell electrons, and that d-electron states are

lying near or crossing the Fermi surface[2]. This character of d electrons is known to be responsible for many peculiar properties of transition metals. In particular, it is shown that the d character in the valence states of transition metals gives rise to so-called local field effects in the first principle formulations of the lattice dynamics of these metals. Further, it has been shown that the effects can be simulated in the phenomenological way, if one treats the transition metal ions as deformable ones. This then becomes a microscopic justification of the shell models to be used for studying the lattice dynamics of transition metals.[3,4]

The first successful applications of the shell models to the lattice dynamical studies of ionic and covalently bonded crystals were made a decade ago[5]. But it is only recently that the shell model found its usefulness in understanding the phonons in transition metals and their compounds.[6,7,8] Hanke and Bilz[6] analyzed the phonon dispersion data of several transition metals for the first time in terms of the shell models. They obtained a result which is in excellent agreements with experiments. However, they did not extend the model to study other lattice dynamical properties of transition metals. In addition, all the transition metals they studied have the face-centered cubic structures except for a couple of metals, Na and Al.

In view of these facts, we consider it interesting to investigate the shell model applicability to the lattice dynamics of body centered cubic transition metals. To do this we have formulated a seven-parameter simple shell model and applied it to analyze the neutron data for the dispersion relations and the lattice specific heat data of chromium, molybdenum, and tungsten. So far, the neutron data for the lattice vibrations in these metals have been analyzed mostly in terms of the force models of the Born-von Karman type[9,10,11]. The force models are found to be satisfactory. However, in order, to have a good fit to the experimental data one must consider at least more than third neighbor interactions. The models then involve a large number of undetermined parameters. In our shell model treatment we have restricted the ion-ion interactions to the second neighbors and, thereby, the model parameters are reduced to seven.

To our best knowledge thus far, the first principle study on the lattice vibrations in bcc transition metals is one made by Animalu[12] who used the transition metal model potential (TMMP) theory. It is observed that, even though his theory can give a satisfactory account of the phonon dispersion data of fcc transition metals, there are large discrepancies between his theory and experiments in bcc transition metals. There is another type of the first principle approach which is successfully applied to Ni and Pd[13]. This latter approach resembles the shell model. But it has not been tested in bcc transition metals. Therefore, it is hoped that our shell model results serve a useful intermediate scheme in such a model approach to the lattice dynamics of bcc transition metals.

2. Formulation of Dynamical Matrix

In the shell model treatment every metal ion is replaced by an ion core of charge Xe and a massless electron shell of charge Ye. The electron shell is assumed to be bound to its ion core by an isotropic spring of

strength k. The sum of the core charge and its own shell charge gives the effective ionic charge $Ze=(X+Y)e$. Two ions in metals are considered to couple with each other through the short range and the Coulomb interactions. The short range interactions are further decomposed into the core-core, the core-shell, and the shell-shell interactions. Denoting these interactions in a usual way the equations of motion of the shell model can be given by[14, 15]

$$\left.\begin{aligned} M\omega^2 U &= (R+ZCZ)U+(T+ZCY)W, \\ 0 &= (T+YCZ)U+(kI+S+YCY)W. \end{aligned}\right\} \quad (1)$$

The notations in equation (1) are quite standard. We followed those in ref. 15. In particular, $R, T,$ and S are 3×3 matrices which specify the short range interactions between the nearest neighbor ions. I is the unit matrix. C represents the Coulomb interaction which can be evaluated by the Ewald method[16]. U and W denote the displacement vectors of the ion core and the associated shell relative to its ion core. M is the mass of the metal ion. Elliminating W in eq. (1), one obtains the shell model dynamical matrix,

$$D=R+ZCZ-(T+ZCY)(kI+S+YCY)^{-1}(T+YCZ). \quad (2)$$

The normal mode frequencies, $\omega_j(q)$, are then determined from the secular equation,

$$\text{det.}\,|M\omega_j^2(q)I-D(q)|=0. \quad (3)$$

In calculating the dynamical matrix D we limited the short range interactions to the second neighbors. The first neighbor interactions are treated as acting only through the electron shells, while we neglected the core-shell and the shell-shell interactions in the second neighbor interactions. It follows then that $R=R_1+R_2$ and $T=S=R_1$. The elements of 3×3 matrices, R_1 and R_2, are given by

$$R_{1xx}(q)=R_{1yy}(q)=R_{1zz}(q)=8\alpha_1(1-C_xC_yC_z),$$
$$R_{1xy}(q)=8\beta_1S_xS_yC_z,$$
$$R_{2xx}(q)=2\alpha_2(1-C_{2x})+2\beta_2(2-C_{2y}-C_{2z}), \text{ and}$$
$$R_{2xy}(q)=0,$$

where

$$C_x=\cos\pi q_x,\ S_x=\sin\pi q_x, \text{ and } C_{2x}=\cos 2\pi q_x,$$

The rest of elements of R_1 and R_2 can be obtained by cyclic permutation of the subscripts, xyz. It must be noted that we have put

$$q=\frac{2\pi}{a}(q_x,q_y,q_z),$$

where a is the lattice constant.

The parameters of simple shell model just discussed consist of five force parameters and two charge parameters. In computing the dispersion frequencies we consistently put the effective ionic charge parameter Z as unity. Therefore, the numerical values of only six parameters need to be determined. The procedure we take is to use three relations between the force parameters and the elastic constants of the metals, and two simple relations between the force parameters and the phonon frequencies, $\omega_L(H)$ and $\omega_{T2}(N)$. Varying the value of Y, we solve the five relations and find the reasonable set of force parameters which give a satisfactory account of the phonon dispersion data. This procedure is, in a sense, very similar to a least squares fitting analysis of the neutron data.

3. Results and Discussions.

Chromium, molybdenum, and tungsten are body-centered cubic transition metals which belong to the column VI of the periodic table. Their neutral atoms have six electrons outside the closed shells and the electronic configurations are $3d^5\ 4s^1$, $4d^5 5s^1$, and $5d^5 6s^1$, respectively[17]. In many respects the meas-

Table 1. Shell Model Parameters

model parameters / transition metals	force constants ($\times 10^5$ dynes/cm)					charge parameter(in units of e)		elastic constants ($\times 10^{11}$dynes/cm^2)		
	α_1	β_1	α_2	β_2	k	Z	Y	C_{11}	C_{12}	C_{40}
Chromium	0.0892	−0.0075	0.34	0.0533	2.3636	1	−2	33.98	5.86	9.9[6]
Molybdenum	0.1118	0.05	0.22	−0.0615	0.4941	1	−1	46	17.6	11[7]
Tungsten	0.2728	0.0932	0.25	−0.0151	8.423	1	−3	53.26	20.49	16.31[8]

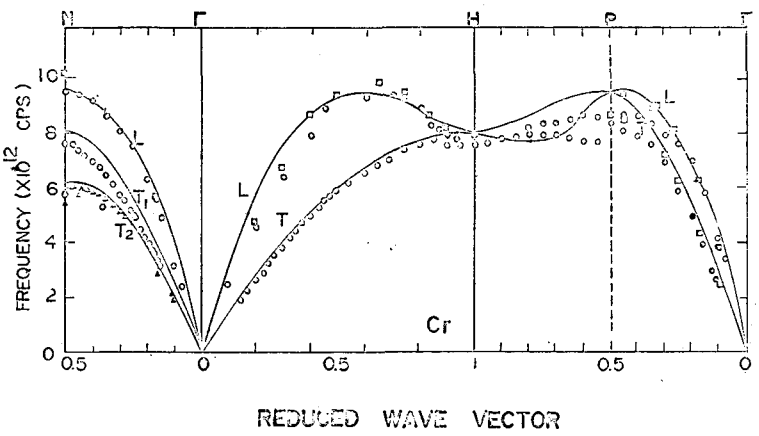


Fig. 1. Dispersion curves for chromium along the principle symmetry directions together with the shell model fit to the neutron data. Circles and triangles are experimental data of Shaw and Muhles tein (ref. 19), while squares and hexagons are those of Møller and Mackingtoshi (ref. 18). White squares and circles denote the longitudinal modes, black ones the transverse or T_1 modes, and black triangles and hexagons T_2 modes. Phonons of T_1 branch have polarization vector parallel to [110] direction, while those of T_2 branch have the polarization vector parallel to [001] direction. Solid curves are the present calculations.

ured phonon spectra for these metals show similarities. In this section we present our shell model results in comparison with other theoretical studies on the latice vibrational properties of them.

1) Chromium

The lattice dynamics of chromium has received much attention in recent years. The first experimental study on the phonon dispersion relations in chromium was made earlier by Møller and Mackingtosh[18]. Recently, Shaw and Muhlestein[19], Cunningham et al.[20], and Muhlestein et al.[21] have also made the neutron measurements for the normal mode frequencies of the lattice vibrations in chromium.

Feldman[9] made the first significant theoretical attempt to calculate the phonon dispersion relations of chromium. He based his study on the fourth neighbor tensor force model of Begbie and Born[22]. It is reportedly known that Gilat[23] also analyzed the neutron data in terms of the seventh neighbor Born-von Karman model. The recent theoretical studies are those of Sharma and Singh,[24] Kesharwani and Agrawal,[25] and Satya Pal.[26] Sharma and Singh used

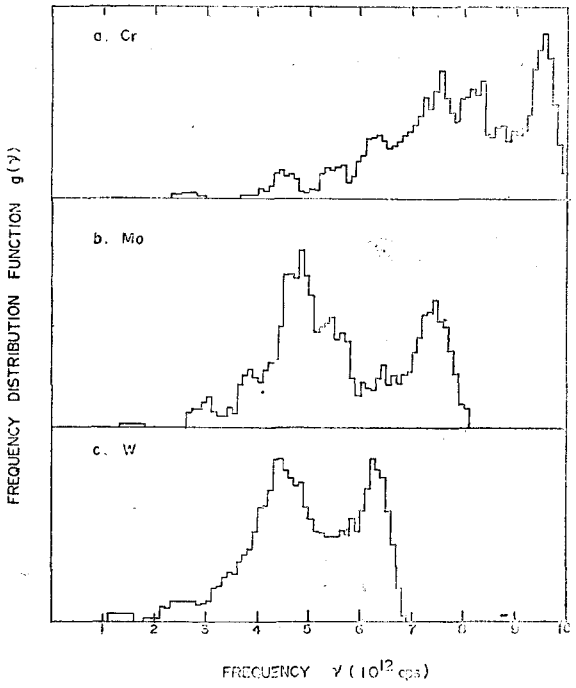


Fig. 2. Frequency distribution functions for chromium (a), for molybdenum (b), and for tungsten (c).

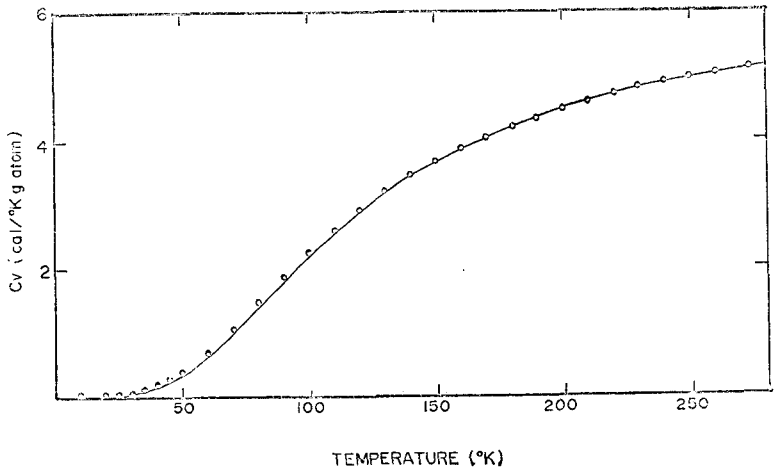
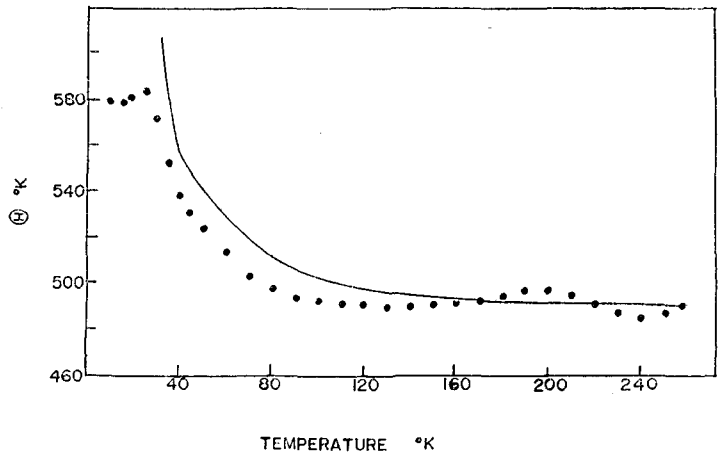


Fig. 3. The lattice specific heat of chromium as a function of temperature. Circles are the experimental data in which the electronic contributions are subtracted.

Cheaveau's model to compute the Debye Waller(DW) factors of chromium. Kesharwani and Agrawal adopted the Krebs model to examine the impurity effects on the lattice vibrations in chromium. Satya Pal applied the Sharma and Joshi model[27] to calculate



FigFig 4. The specific heat Debye temperature of chromium versus temperature. The circles are taken from the work of Clusius and Franzosini (ref. 28). The solid line represents the present calculation.

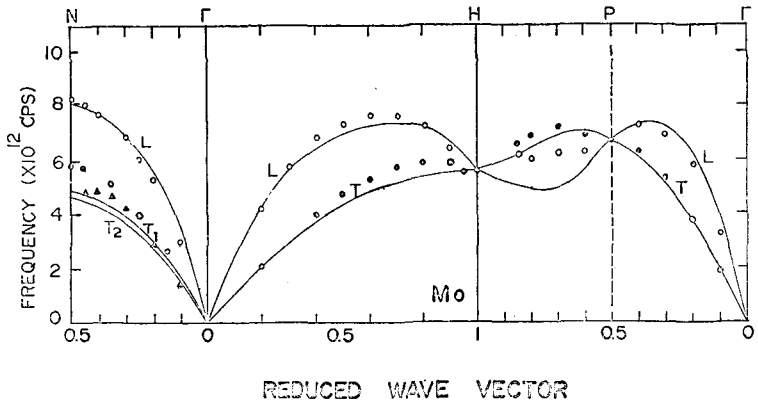


Fig. 5. Dispersion curves for the lattice vibrations in three major directions in molybdenum at 296K°. Circles and triangles are experimental points among which open circles denote the longitudinal modes, solid circles the transverse T_1 modes, and triangles the T_2 modes. Solid curves denote the shell model calculations.

the lattice dynamical properties of this metal. Among these, Feldman's study is a most extensive one. He obtained an excellent fit to the measured phonon frequencies. However, his results are not to be expected, considering that interactions between rather far-distant neighbor ions are taken into account. Satya Pal's study is the most recent one. But the model he used is not consistent with the lattice translational symmetry and, thereby, the frequencies computed from the model are not periodic in the reciprocal space. Besides these, we should mention the work of Animalu[12], who

applied the TMMP theory to calculate the phonon dispersion relations of chromium. This is regarded as the first microscopic study made in chromium. Unfortunately, some discrepancies found between his results and experiments.

In view of these facts, we felt that it is interesting to reconsider the lattice dynamics of chromium in terms of the simple shell model formulated in section 2. In this model application we initially put $Y=-Z$ and fitted the five force parameters to three elastic constants and two dispersion frequencies, ω_L (H) and ω_{T2}(N). It is found that the force parameters determined this way predicted too high or too low frequencies in the [110] directions. Therefore, it becomes necessary to readjust the force parameters by varying the value of Y, until a good a greement between the frequency calculations and neutron data is observed. The numerical values of the model parameters thus obtained are listed in table 1. An alternative procedure would be to use all the measured frequencies across the Brillouin zone in a least square fit.

The phonon dispersion curves of chromium are shown in Fig. 1 together with the shell model calculations. There are some differences between the neutron data of Møller and Mackingtosh and those of Shaw and Muhlestein particularly at or near the Brillouin zone boundary. Nevertheless, the overall agreements of calculations with experiments are seen to be reasonably good. Figure 2a is the frequency distribution function calculated by the root sampling method. In this calculation we diagonalized the dynamical matrix at 47 inequivalent points within the irreducible segment of the first Brillouin zone. This corresponds to 10^3 sampling points inside the Brillouin zone. We then collect the frequencies in the frequency interval of 0.1×10^{12} Hz. The frequency distribution function, $g(\nu)$, is then used for computing the specific heat of chromium as a function of temperature. This result is shown in Fig. 3 and the result is also presented as a Debye T curve in Fig. 4. It must be noted that the electronic contributions to the specificheat is subtracted in these curves[28]. Even though we have not compared our results with other model calculations in Figs. 3 and 4, better agreements with experiments are observed in our shell model calculations[26].

2) Molybdenum

The phonon dispersions of molybdenum were first determined by Woods and Chen[10] with the help of the coherent one phonon scattering of thermal neutrons. Recently, Powell et al.[29] also reported the similar neutron measurements. Woods and Chen made the Born-von Karman analysis of their neutron data in terms of both general and axially symmetric force models. They found that, if more than third neighbor interactions are included in their force models, the qualitative features of the measured phonon dispersion curves can be explained.

Mahesh and Dayal,[30] Kesharwani and Agrawal[31], and Animalu[12] have also studied the lattice dynamics of this metal. Mahesh and Dayal modified the Krebs model by including the third neighbor central interaction. Then they used the model to compute the lattice vibrational frequencies and the Debye temperature of molybdenum, and obtained qualitatively good results. Kesharwani and Agrawal based their study on the Krebs model with the second neighbor ionic interactions. But they concentrated on the study of impurity effects on the lattice

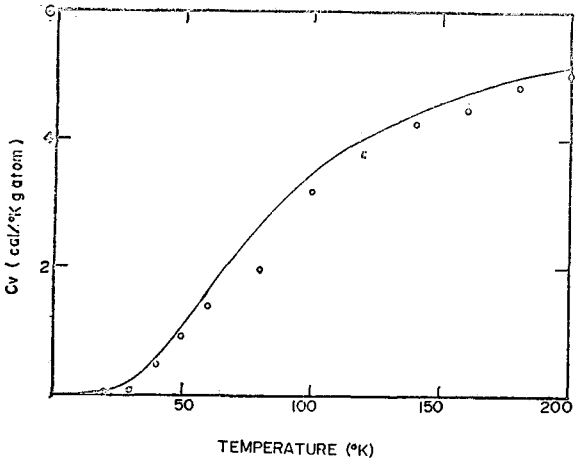


Fig. 6. The lattice specific heat of molybdenum versus temperature.

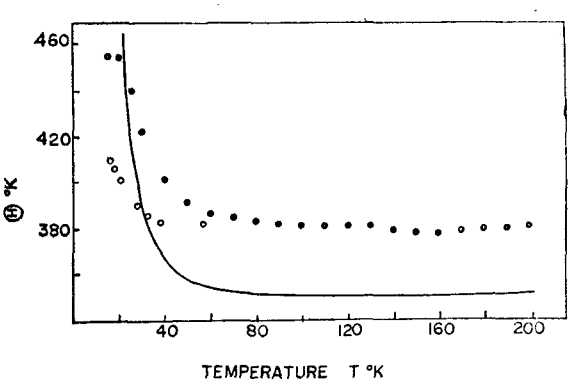


Fig. 7. The specific heat Debye temperature versus temperature for molfbdenum.

specific heat of the molybdenum alloy. Finally, Animalu attempted the first microscopic study on the lattice vibrations in this metal by the TMMP theory. As mentioned already, his results turned out to be very qualitative.

In view of the success of our shell model shown in chromium and due to interest in the model applicability, we reformulated the lattice dynamics of molybdenum in terms of the simple shell model. To begin with, the numerical values of the model parameters are determined by the similar procedures that we have taken in the chromium case. Namely we have made use of the elastic constants and two phonon frequencies at the Brillouin zone boundary points, N and H. The relation $Y=-Z$ is used. The elastic constants were taken from the ref. 32 and the phonon frequencies from the work of Woods and Chen[10]. The numerical results are given in Table 1.

In Fig. 5 the shell model calculations are compared with the dispersion curve measurements of Woods and Chen. The agreements between the calculations and experiments are shown to be generally good. But the calculated frequencies of the T_1 branch are found to be about 15% lower than the measured frequenties. Woods and Chen noted that their neutron data show a pronounced anomaly near the point H in the dispersion curves. In fact, they excluded the neutron data at all the points near H with $5>0.9$ from the least squares fitting analysis. In contrast with this we forced the shell model parameters to fit the phonon frequency at the point H. This requirement may be responsible for the discrepancies observed in our calculations. Therefore, it seems possible to improve the fit of the present shell model to the dispersion data a little better. To do this one can employ the least squares fitting method with or without the neutron data around H. Also one can lift the assumption $Y=-Z$ and $Z=1$, since the effective ionic charge and the shell charge of molybdenum are not known at the present time.

Fig. 2b is the frequency distribution function, $g(\nu)$, which is obtained by the root sampling method. As in the case of chromium, 10^3 sampling points in the Brillouin zone are selected for this calculation. $g(\nu)$ is used for the evaluation of the lattice specific heat or equivalently the specific heat Debye

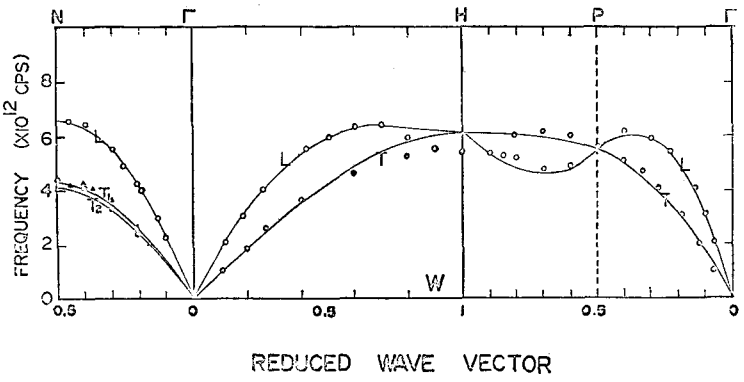


Fig. 8. Phonon dispersion curves for tungsten at room temperature. Experimental points and notations have the same meaning as those in Fig. 5. Solid curves denote the shell model calculations.

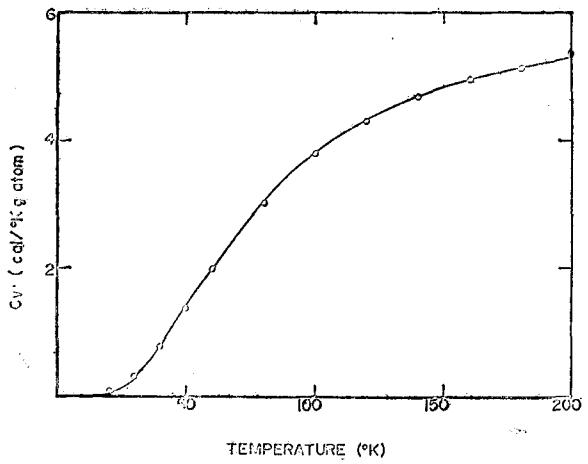


Fig. 9. The lattice specific heat of tungsten versus temperature.

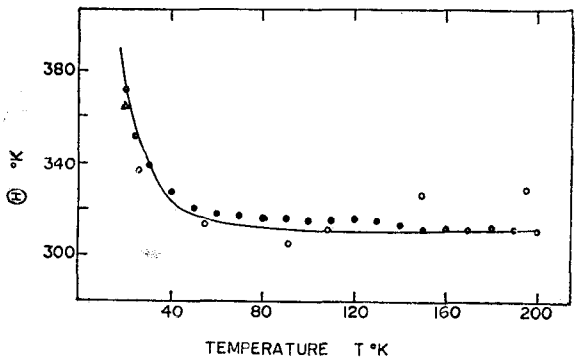


Fig. 10. The specific heat Debye temperature versus temperature for tungsten.

temperature of molybdenum. The results are presented as the specific heat versus temperature in Fig. 6 and as the Debye temperature versus temperature in Fig. 7. It is shown that the shell model predicts a little higher values of the specific heat. It is presumed that this discrepancy is also the result of the dissatisfactory fitting of our shell model parameters to the dispersion data of molybdenum. Therefore, improvements in the shell model fits need to be made in order to have better account of the specific heat data of molybdenum.

3) Tungsten

The lattice dynamics of tungsten has been investigated by many authors.[11, 12, 30, 33] Chen and Brockhouse[11] measured the phonon dispersion curves in the three major directions of this metal by the neutron inelastic scattering experiment. They made a Born-von Karman general force model analysis, and found that the qualitative features of their neutron data can be explained by a third neighbor force model. Also they noted that the measured values of the elastic constants[34] satisfy the condition of isotropy and, thereby, two transverse phonon modes pro-

agating in the [110] direction must be degenerate with the second neighbor force model. Since this is not the case, they concluded that the interaction forces must extend beyond the second neighors.

Recently, Mahesh and Dayal[30], Shukla and Animalu[12] also reported their investigations on the lattice vibrations in tungsten. Mahesh and Dayal[30] modified the Krebs model by including the third neighbor central interaction. They computed the phonon dispersion relations and the lattice specific heat of tungsten, and obtained a good agreement between the model calculations and experiments. Animalu studied the lattice dynamics of tungsten based on the TMMP theory. This is the first microscopic study. Unfortunately, as in cases of other bcc transition metals, his result is far from being satisfactory.

It is noted that the above situations in the lattice dynamical study of tungsten are very similar to those of molybdenum. Therefore, motivated similarly as in the molybdenum case, we reexamined the lattice dynamics of tungsten in terms of the simple shell model. As before, the model parameter values are fitted to the elastic constants[34] and the measured phonon frequencies at the points N and H. It is found that $Y=-3$ for the shell charge parameter of tungsten gives a reasonable fit to the phonon dispersion data. In addition, we found an improvement in the shell model fit to the dispersion data, when we made a slight readjustment of the force parameter values independently of the exact relations between the force parameters and the phonon frequency at the point H. Table. 1 shows the numerical results thus obtained.

In Fig. 9 the shell model dispersion relations are compared with the measured ones. Th discrepancies between the calculations and the phonon data near H are caused by the readjustment of the force parameter values in the way that we discussed just before. Figure 2*c* represents the frequency distribution function of tungsten obtained from the frequency calculations at the 10^3 sampling points in the Brillouin zone. It is observed that the distribution function exhibits two pronounced peaks at 4.5 and 6.3×10^{12} Hz. Two peaks are also observed in other model studies[11, 30]. Chen and Brockhouse[11] found two peaks at 4.6 and 6.3×10^{12}Hz in their 8th-neighbor force model of 23 parameters. Also, Mahesh and Dayal[30] observed the peaks at 4.6 and 6.4×10^{12} Hz in their modified Krebs model calculation. Using the distribution function of Fig. 2c, we finally calculated the lattice specific heat and compared the results with the measurements of Clusius and Franzosini[35] in Fig. 10 and 11. It is shown that the shell model results agree remarkably well with the specific heat data of tungsten. Therefore, it is suggested that the model should be useful for studying other lattice dynamical properties of tungsten such as Debye Waller factor and the impurity effects.

4) Conclusions

Phenomenologically speaking, the transition metals have two special features in them. Since they are metal, some of the valence electrons are freed to participate in the dynamic screening process of the Coulomb interactions between the metal ions. In addition, they possess the d-shell electrons which are not rigidly bound to their ion core. Therefore, the transition metal ions can be regarded as deformable ions rather

than rigid ions. In this paper we have concentrated on this deformable nature of the transition metal ions, and presented a simple shell model analysis of the lattice vibrations in chromium, molybdenum, and tungsten. We have computed the phonon dispersion relations, freguency distribution functions, and the lattice specific heats of these metals, using a seven-parameter shell model. It is assumed that the effective ionic charge is unity. This assumption is not essential. But it is made for the model simplfication. The rest of the model parameter values is adjusted to fit the elastic constants and the measured phonon frequencies.

In the case of molybdenum the shell model predicts higher values of the specific heat than the measurement. It is attributed to the fact that our shell model fit to the neutron data for the dispersion relations is not complete. Therefore, it is suggested that the least squares fitting analysis of the phonon frequencies over the whole Brillouin zone may improve the present results far better. It is also suggested that one can lift the assumption, $Z=1$, since the effective ionic charge of molybdenum is not precisely known at the present time. For cases of chromium and tungsten the agreements between the shell model calculations and the experimental data are found to be excellent. Therefore, it is concluded that our shell model would be useful for the lattice dynamical study on other bcc transition metals.

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