Angular Forces and Normal Vibrations in Platinum

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(Z. Naturforsch. **32a**, 1490—1494 [1977]; received July 23, 1977)

A lattice dynamical study of platinum has been made on the basis of the improved Clark-Gazis-Wallis model considering volume forces of Krebs' nature. The phonon dispersion relations obtained for the three symmetry directions have been compared with the recent inelastic neutron scattering experiments. The specific heat at constant volume has been calculated by Blackman's root sampling technique for temperatures above $\Theta/10$, and below this temperature the calculations are carried out by employing the modified Houston spherical six-term integration procedure. The computed lattice specific heats in terms of the effective Debye temperatures Θ are compared with the available calorimetric data. The theory is in good agreement with the experimental data.

1. Introduction

In the recent past, Overton[1] has made quantitative calculations on the contribution of different electron gas energies to the bulk modulus. While discussing the case of copper, he infers that the non-central forces between the ions might also account for part of the Cauchy discrepancy and expects this contribution to increase with increasing ionic size. In confirmation of these ideas, we have recently employed the modified Clark, Gazis, and Wallis (CGW) non-central force approach[2,3,4] to study the influence of angular forces on the lattice dynamic of noble metals[5]. These investigations were found to be in favour of the conclusions drawn earlier by Overton[1] from his studies for copper, and the theory is found to be in excellent agreement with the experimental observations, demonstrating thereby that the angular forces play a dominant role in the case of this cubic structure. Since the transition metals are associated with large ionic sizes, the contribution of ion-ion angular non-central force interactions to the Cauchy discrepancy may also there be significant. It therefore seemed worthwhile to study the crystal dynamics of an fcc transition metal using the modified CGW scheme in which the presence of ion-ion angular interactions has adequately been taken into account on the lines of Clark, Gazis, and Wallis[6]. We have selected platinum for this purpose, because the departure from the Cauchy relation is greater for platinum than for copper and one can surmise that angular forces are more important in platinum than in copper.

In the present work the phonon dispersion, frequency spectrum, and specific heat of platinum, has been calculated. The assumed scheme of the calculations[2,3] has originally been considered by Shukla and Closs[2] to compute the phonon dispersion of copper, and was subsequently modified by the present authors[3] for bcc metals. This model is superior to other lattice dynamical approaches[7–9] in the sense that it also satisfies the symmetry requirements of the lattice and that therefore the frequencies obtained are periodic in the reciprocal space. It is to be emphasized[4] that the Cauchy discrepancy in cubic structures arises from the volume forces in addition to angular interactions of the usual CGW nature. This modification of the original CGW model seems to be essential because the presence of the electron gas forms an integral part of the lattice interactions and should be adequately taken into account in a lattice dynamical approach.

2. Secular Determinant

The phonon frequencies can be obtained from the secular equation

$$|D(\boldsymbol{q}) - 4\,m\,\pi^2\,\nu^2\,I\,| = 0 \qquad (1)$$

where $\boldsymbol{D}$ is a 3×3 dynamical matrix, $\boldsymbol{I}$ the unit matrix, and m the ionic mass. The explicit expressions for the typical elements of $\boldsymbol{D}$ in the fcc structure are

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$$\begin{aligned} D_{11}(\boldsymbol{q}) = {} & 2\left[\alpha_1 + \frac{8}{a^2}(\gamma_1+\gamma_2)\right][2 - \mathrm{C}_1(C_2+C_3)] + 4\,\beta_1 S_1^2 \\ & - \frac{4\,\gamma_1}{a^2}(2\cos 2\,\pi\,a\,k_1 - \cos 2\,\pi\,a\,k_2 - \cos 2\,\pi\,a\,k_3) \\ & + A\sum_{\boldsymbol{G}}\left[\frac{(\boldsymbol{q}+\boldsymbol{G})_1\,(q+\boldsymbol{G})_1}{|\,\boldsymbol{q}+\boldsymbol{G}\,|^2+k_c^2}\,g^2(|\,\boldsymbol{q}+\boldsymbol{G}\,|\,r_s) - \frac{G_1^2}{|\,\boldsymbol{G}\,|^2+k_c^2}\,g^2(|\,\boldsymbol{G}\,|r_s)\right]; \end{aligned} \tag{2}$$

$$D_{12} = \left(2\,\alpha_1 - \frac{16\,\gamma_1}{a^2}\right)S_1\,S_2 + A\sum_{\boldsymbol{G}}\left[\frac{(\boldsymbol{q}+\boldsymbol{G})_1\,(\boldsymbol{q}+\boldsymbol{G})_2}{|\,\boldsymbol{q}+\boldsymbol{G}\,|^2+k_c^2}\,g^2(|\,\boldsymbol{q}+\boldsymbol{G}\,|\,r_s) - \frac{\boldsymbol{G}_1\,\boldsymbol{G}_2}{|\,\boldsymbol{G}\,|^2+k_c^2}\,g^2(|\,\boldsymbol{G}\,|r_s)\right], \tag{3}$$

where $C_1 = \cos\pi\,a\,k_1$, $S_1 = \sin\pi\,ak_1$, $g(x) = \dfrac{3\,(\sin x - x\cos x)}{x^3}$,

k_1, k_2, k_3 are the components of $\boldsymbol{k}$ in cartesian coordinates, a is the lattice constant, $\boldsymbol{G}$ the reciprocal lattice vector, α_1 and β_1 are the central force constants and γ_1 and γ_2 the angular force constants upto the second neighbours. The $g(x)$ function introduced above is arbitrary to reduce the effect of large $\boldsymbol{G}$ values. The screening parameter k_c is given by

$$k_c{}^2 = k_c{}^2(P)\,f(t)\,,$$

where $k_c(P)$ is the screening parameter of Pines:

$$k_c{}^2(P) = 0.353\,(r_s/a_0)^{1/2}\,k_F\,.$$

Here $r_s = (3/4\,\pi\,n_e)^{1/3}$ is the interelectronic spacing, n_e the electron density, a_0 the radius of Bohr, and

$$f(t) = \frac{1}{2} + \frac{1-t^2}{4t}\,\mathrm{In}\,\frac{1+t}{1-t}\ \text{with}\ t = k/2k_F\,.$$

3. Numerical Computation

The phonon dispersion relations at room temperature along the three symmetry directions [ζ00], [ζζ0], and [ζζζ] of platinum are determined from the solutions of the secular equation (1) along these directions. The frequency distribution of the normal modes of vibration have been computed by Blackman's root sampling technique[10] for a discrete subdivision in wave-vector space. For this purpose, it is essential to determine the characteristic frequencies at a suitable number of points in an irreducible section of the first Brillouin zone. We have considered an evenly distributed mesh of 8000 wave vectors in the first Brillouin zone. From Born's cyclic boundary condition and considerations of lattice symmetry, these 8000 points reduce to 262 non-equivalent points including the origin lying within 1/48th part of the Brillouin zone and weighted according to the number of similar points associated with them. The 24000 frequencies corresponding to 8000 points in the zone were obtained from the solution of the secular equation of the modified CGW model for an fcc lattice. These frequencies represent the complete vibration spectrum. The number of frequencies lying in intervals of $.13\times10^{12}$ (c/s) were counted, and from these values the frequency distribution of platinum was plotted. Using the computed frequency spectrum, the contribution of lattice vibrations to the specific heat per gram atom, i.e. C_v was obtained from the numerical integration of the usual relation.

$$C_v = 3\,R\int_0^{\omega_m} E(\hbar\,\omega/k\,T)\,G(\omega)\,\mathrm{d}\omega \tag{4}$$

where ω_m the maximum frequency and $E(\hbar\,\omega/kT)$ the Einstein specific heat function. This method was used at moderate temperatures down to $0.1\,\Theta$ as $G(\omega)$ calculated by the sampling method can not be very accurate in the low-frequency range and because of the coarseness of the mesh used. For temperatures below $0.1\,\Theta$, where the lower frequencies have a predominant influence, we used Houston's method[11] as elaborated by Horton and Schiff[12]. The frequency distribution function can be written as

$$G(\omega) = \left(\frac{1}{2\,\pi}\right)^3\int\sum_p\left(q^2\,\frac{\mathrm{d}q}{\mathrm{d}\omega}\right)_p\mathrm{d}\Omega_q\,, \tag{5}$$

where Ω_q is the solid angle in the wave vector space and the summation over p is on the three modes of

Table 1. Constants for platinum used in the calculations.

Metal	Elastic constants (10^{11} dyn/cm^2)			Lattice Parameter (Å)	Density (gm/cm^3)	T (°K)
	C_{11}	C_{12}	C_{44}			
Platinum[a]	34.67	25.07	7.65	3.9237	21.445	300

[a] R. E. Macfarlane, J. A. Rayne, and C. K. Jones, Phys. Letters **18**, 91 (1965).

lattice vibrations for each $\boldsymbol{q}$. Use of (4) in (5) gives

$$C_v = \frac{3\,R}{(2\,\pi)^3} \sum_p \int_0^{q_{\max}} \int_{\Omega_q} E\left(\frac{\hbar\,\omega_p}{k\,T}\right) q^2\,\mathrm{d}q\,\mathrm{d}\Omega\,. \qquad (6)$$

For the evaluation of C_v from (6), the integration over $\boldsymbol{q}$ was performed numerically and the angular integration was carried out by a modified Houston's six-term interpolation procedure. The six directions of $\boldsymbol{q}$ used are: [100], [110], [111], [210], [211] and [221]. The weights of these directions were obtained from Betts et al.[13] and are given by the coefficients of I_α in the equation

$$J_\alpha = \frac{4\,\pi}{1081080}\,[117603\,I_{\mathrm{A}} + 76544\,I_{\mathrm{B}} + 17496\,I_{\mathrm{C}} + 381250\,I_{\mathrm{D}} + 311040\,I_{\mathrm{E}} + 177147\,I_F]\,. \qquad (7)$$

The numerical values of the elastic constants and other parameters used in the calculations are listed in Table 1.

4. Results and Discussion

Phonon Dispersion

Phonon dispersion measurements for platinum at room temperature have been made by Orlich and Drexel[14]. However, the results of these workers are somewhat incomplete. Complete dispersion curves of platinum at 90 K have been recently measured by Dutton et al.[15] by the technique of inelastic scattering of thermal neutrons along the three symmetry directions. The T_1 branch in the [$\zeta\zeta 0$] direction shows a kink and the other branches agree well with the results of Orlich and Drexel. Data of the experiment carried out by Dutton et al.[15] are plotted in Fig. 1 along with the theoretical values of our non-central force approach. The theory is in reasonably satisfactory agreement with the experiment.

Frequency Distribution

Dutton et al.[15] have derived the frequency distribution of platinum from the force constants of the sixth neighbours model using the method of Gilat and Raubenheimer[16]. The calculation assumes that the force constants derived from fitting measurements in the symmetry directions are sufficient to predict the correct frequencies at off-symmetry-points in reciprocal space. These measurements show that the first neighbour forces are dominant but relatively large forces exist out to fourth neighbours. The longer range forces are much weaker.

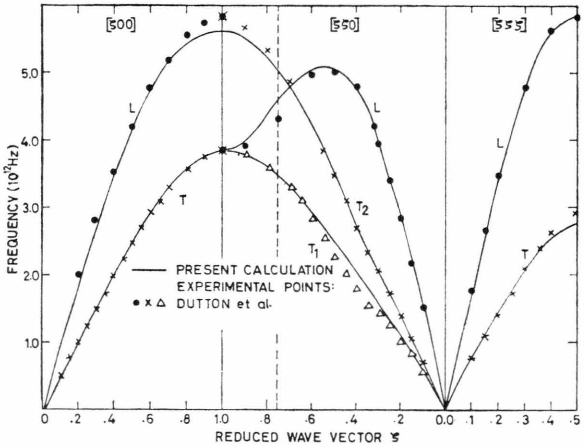

Fig. 1. Phonon dispersion curves for Platinum along the symmetry directions.

The observations of Dutton et al. are shown in Fig. 2 along with our calculated results. From Fig. 2 it is evident that the computed $G(\nu)$ agrees in its broad features with the experimental spectrum. The high and low frequency peaks are almost at the same positions and the computed high frequency peak has almost the same intensity as the observed one. The observed low frequency peak however is somewhat higher than the theoretical one. In addition, the computed frequency distribution corresponds to a broad maximum, the high frequency peak being higher than the low frequency one, whereas the experimental curve has sharp maxima with the high frequency peak being lower.

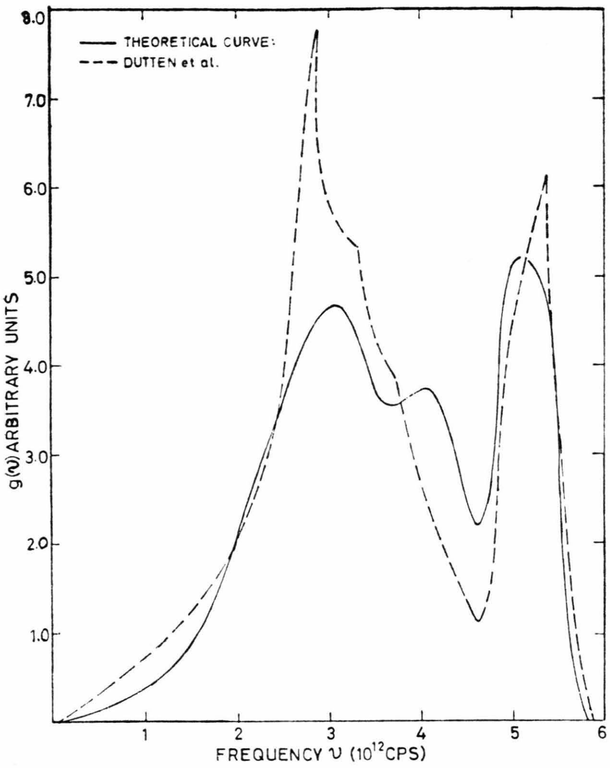

Fig. 2. Frequency spectrum of Platinum.

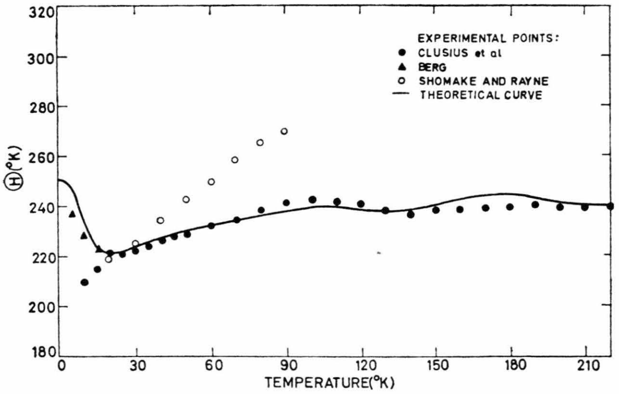

Fig. 3. Debye temperature of Platinum as a function of temperature.

Specific Heat

The specific heat of platinum has been measured by several investigators[17–24], but the data of only two[19, 23] extend to temperatures greater than 25 K. Among these observations, the measurements of Clusius et al.[19], taken in the temperature range 10—300 K, are more detailed than those of Shoemake and Rayne[23] taken only in the temperature range 10—100 K. To calculate the lattice specific heat, Clusius et al. and Shoemake and Rayne have used different values of the electronic specific heat coefficient γ. Further, these investigations have assumed a constant value of γ over the whole temperature range. Recently, however, Shimizu and Katsuki[25] have found that the value of γ decreases by about 20% in the range $0 < T < 300$ K. Following Shimizu and Katsuki's method, Konti[26] has calculated the Θ values corresponding to the specific heat values of the above mentioned two investigators[19, 23]. The value of the electrinic specific heat coefficient used for subtracting the contribution of the electronic specific heat from the lattice specific heats is $(1555 - 114.9 \times 10^{-2}\, T + 172.8 \times 10^{-6}\, T^2)$ cal/deg² gm atom. These values are shown in Fig. 3 together with some low temperature results due to Berg[24] taken in the temperature range 2.6—20 K. There is, however, a considerable difference between the measurements of Clusius et al. and Shoemake and Rayne. This discrepancy may possibly be attributed to the difference in the of purity of specimens. It is evident from Fig. 3 that the computed $\Theta - T$ values are in good agreement with the experimental observations. The Θ values are particularly in close accord with the measurements of Clusius et al.

A perusal of Figs. 1—3 shows that the theory of the modified CGW approach is reasonably consistent with the experiments. This proves the adequacy of the modified CGW formalism for the dynamical description of platinum. Evidently the angular forces play an important role in the crystal dynamics of this cubic structure and should be adequately taken into account. It has been demonstrated in the present investigation that the Cauchy discrepancy can be attributed to two types of non-central force interactions taking place inside the crystal lattice. The first one originates from the non-central forces between the ions, and the second one arises from the electronic-ion dynamical matrix elements. As far as the agreement of our calculations with the experiments is concerned, the present authors are definitely in favour of the theoretical prediction made by Overton from his studies on copper.

Acknowledgements

The authors are highly thankful to Dr. S. Chandra and Mr. V. P. Singh for helpful suggestions during the course of these investigations. One of us (H.L.K.) is also thankful to C.S.I.R. India for financial assistance and the authorities of I.I.T. Computer Centre, Kanpur, for providing the facilities of their IBM 7044 computer.

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