Lattice Dynamics of Gold

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Abstract: *A phenomenological model for the lattice dynamics of gold metal is developed. The total interaction inside the metal is composed of mainly the interactions between the ions and the interaction between the ions and electrons. A many parameter potential corresponding to two-body and three-body interactions is introduced to describe the forces between ions. The contribution to the potential energy from ion-electron interaction is considered by a screened Coulomb potential. The theoretical model developed is employed to obtain the phonon dispersion curves of gold. Computed phonon frequencies are used to explain the Debye characteristic temperatures at different temperatures. The computed results for phonon dispersion curves and Debye characteristic temperatures compare satisfactorily with the experimental results.*

Keywords: ***Phonon Dispersion Curve, Phenomenological Model, Screened Coulomb Potential, Specific Heat, Debye Characteristics Temperature, Femtosecond.***

1. Introduction

A number of lattice dynamical models have been developed for the study of lattice dynamics of metals. As the exact calculation of the lattice

dynamical properties of metallic solids is a very difficult work, a number of assumptions have been introduced in developing the theories for the calculation of the vibrational frequencies of metals. Also the first principle theory and phenomenological theories and models have been developed for the lattice dynamical study of gold.

Various phenomenological theories and models have been proposed and applied to the study of lattice vibrations of metals. The phenomenological models are mainly the de Launay type model, Clark, Gazis and Wallis[1] type model and the valence force field model. These force models have been applied by Awasthi and Kushwaha[2], Rammurthy and Satishkumar[3] and Thakur and Singh[4] to the study of lattice vibration of metals.

Gold has some most interesting properties. It is a highly anisotropic metal in which departure from the Cauchy relation is the highest. The atomic volume and the shear constant C_{44} and C_{11}-C_{12} are nearly the same as in the case of silver, but the bulk modulus is very high. Less attention is paid to the theoretical lattice dynamical studies of this metal in the past due to paucity of experimental measurements. Earlier, some workers[5-6] investigated the lattice dynamics of gold by the phenomenological models, whereas others[7-8] performed the calculation of phonon dispersion curves of gold based on model potential or pseudopotential approaches. Also, phonon dispersion relations of gold are studied by Kumar and Hemker[5] using short range paired forces in conjunction with Krebs model for ion-electron interaction.

Recently Kolomenskii et al[9] presented the Femtosecond electron- lattice thermalization dynamics in a gold film probed by pulsed surface Plasmon resonance. They have discussed the thermalization of the electronic subsystem and energy transfer to the lattice are discussed in connection with the two-temperature relaxation model that takes into account temperature dependences of the electronic heat capacity and the electron-phonon coupling.

The recent investigations on theoretical and experimental study of gold metal and its compounds on properties related to gold nanoparticles, silver electroplating and anharmonic lattice

vibrations motivated the present study of lattice dynamics of gold. The results obtained on lattice vibrations of perfect crystal lattice are useful in predicting the properties of real crystals. In the present work a theoretical model which considers the two-body and three-body ion-ion interaction and incorporates the ion-electron interaction has been developed. The dynamical matrix developed in the present work is solved to obtain the phonon dispersion curves, specific heat and Debye characteristic temperatures for gold. The theoretical results have been compared with the available experimental data.

2. Methodology

The elements of the dynamical matrix are written as

$$D(\vec{q}) = [D(\vec{q})]^{\text{i-i}} + [D(\vec{q})]^{\text{i-e}} \quad (1)$$

The superscripts i-i and i-e represent the ion-ion and ion-electron interactions respectively.

The elements of the dynamical matrix corresponding to ion-ion interaction have been obtained employing the extended Morse[10] potential involving two-body and three-body potentials. These elements of dynamical matrix obtained in the present work are

$$D^{\text{i-i}}(\vec{q}) = D^{(2)}(\vec{q}) + D^{(3)}(\vec{q}) \quad (2)$$

Where $D^{(2)}(\vec{q})$ and $D^{(3)}(\vec{q})$ are the elements of dynamical matrix for two-body and three-body interactions respectively given as:

$$D^{(2)}_{\alpha'\beta'}(\vec{q}) = 2(\beta_1 - \alpha_1) S_{\alpha'} S_{\beta'} \quad (3)$$

$$D^{(2)}{}_{\alpha'\alpha'}(\vec{q}) = 4\beta_1 + 8\alpha_1 - 2(\alpha_1 + \beta_1) C_{\alpha'}(C_{\beta'} + C_{\gamma'}) - 4\alpha_1 C_{\beta'} C_{\gamma'} + 4\beta_2 S^2_{\alpha'} + 4\alpha_2 (S^2_{\beta'} + S^2_{\gamma'}) \quad (4)$$

$$D^{(3)}{}_{\alpha'\alpha'}(\vec{q}) = 8\beta_1(2 - C_{2\alpha'}) - 4\beta_3[C_{\alpha'}(C_{\beta'} + C_{\gamma'})] \quad (5)$$

and

$$D^{(3)}{}_{\alpha'\beta'}(\vec{q}) = 4\beta_3[C_{\alpha'}(C_{\beta'} + C_{\gamma'})] - 8\beta_3 C_{2\beta'} \quad (6)$$

where α', β' and γ' stand for the cartesian components along X, Y and Z-axis respectively. α_1 and β_1 stand for the two-body force constants for the first neighbours and α_2 and β_2 stand for force constants for the second neighbours respectively. Also $S_{\alpha'} = sin(aq_{\alpha'}), C_{\alpha'} = \cos(aq_{\alpha'}), C_{2\alpha'} = \cos(2aq_{\alpha'}) and \beta_3$ is force

constants corresponding to three-body potential, *a* being the half lattice parameter.

The elements of the dynamical matrix corresponding to ion-electron interaction have been taken as reported by Mishra and Singh[11].

The three elastic constants of the FCC metals are expressed in terms of the model parameters by expanding the secular determinant in the limit of long wavelengths. The relation between the model parameters including the bulk modulus of electron gas and the three elastic constants of FCC metals are obtained as:

$$C_{11}=\frac{1}{2a}[2(\alpha_1+\beta_1)+4\beta_2+20\beta_3]+K_e \tag{7}$$

$$C_{12}=\frac{1}{2a}[-5\alpha_1+\beta_1-4\alpha_2]+K_e \tag{8}$$

$$C_{44}=\frac{1}{2a}[3\alpha_1+\beta_1+4\alpha_2+2\beta_3] \tag{9}$$

where K_e is the bulk modulus of electron gas.

Numerical values of model parameters are obtained using experimental values of three elastic constants[12] and following phonon frequencies at $[\xi 00]$ for longitudinal and transverse modes:

$$m\omega_L^2(X)=8\alpha_1+8\beta_1+16\beta_3+D_{11}^{i-e} \tag{10}$$

and

$$m\omega_T^2(X)=12\alpha_1+4\beta_1+8\beta_3 \tag{11}$$

where D_{ij}^{i-e} is the matrix element at $[\xi 00]$ corresponding to electron-ion interaction. The input data for evaluating the model parameters for silver and their numerical values are given in Tables 1, 2 and 3.The model parameters given in Table 3 have been used to calculate the phonon dispersion curves along three principal symmetry directions $[\xi 00],[\xi\xi 0]$ and $[\xi\xi\xi]$ of the first Brillouin zone for gold. The values of C_v at different temperatures are obtained from $C_v=\frac{3R}{3000}\sum_{\upsilon}E(\frac{h\upsilon}{KT})g(\upsilon)$,Where $g(\upsilon)$ is the frequency distribution function for the metal, R is the gas constant and $E(h\upsilon/kT)$ is the Einstein function defined by

$E(x) = x^3 e^x / (e^x - 1)^2$, Where $x = h\upsilon / kT$. The computed values of C_v at different temperatures are then used for evaluating the Debye characteristic temperatures.

Table 1. Input Data used for the Determination of Model Parameters

Element	Elastic Constants 10^{10} Nm-2			Reference for Elastic Constant	Phonon frequencies 10^{12} s-1		Reference for phonon frequencies
	C11	C12	C44		νLO	νTO	
Gold	12.23	16.31	4.19	[12]	4.61	2.75	[13]

Table 2. Values of Physical Quantities used in the Calculations

Element	Atomic Radius 10^{-10} m	Lattice Constant 10^{-10} m	Atomic Mass 10^{-27} kg	F. S. Wave Vector KF 10^{-1} m	Screening Multiplication Constant σ
Gold	1.592	2.035	316.965	1.204	0.353

Table 3. Values of Model Parameters and Electron Bulk Modulus

Element	Force constants (Nm^{-1})					Bulk modulus K_e 10^{10} Nm^{-2}
	α_1	β_1	α_2	β_2	β_3	
Gold	-3.24	36.7086	–1.639	7.6419	-1.6794	5.234

3. Results

Lynn et al[13] were able to measure the phonon frequencies of gold along principal symmetry directions at room temperature by the coherent inelastic scattering of neutrons. The results obtained are compared with the experimental data of Lynn et al[13] in Figure 1. The agreement of the present theoretical results with the experimental values is quite good. The dispersion curves along symmetry directions $[\xi 00],[\xi\xi 0]$ and $[\xi\xi\xi]$ of gold have been computed by solving the Secular determinant developed on the basis of the phenomenological model in the present work. The results of phonon dispersion curve along symmetry directions $[\xi 00],[\xi\xi 0]$ and $[\xi\xi\xi]$ have been presented in Figure 1 and are also comparable with those of Thakur and Singh[14]. Among the several earliest measurements of specific heat of

gold, the measurement by Clusius and Hartek[15] are important. The specific heats and Debye characteristic temperature of gold have been computed by applying the present theoretical model. The computed values of specific heat at different temperatures are used to obtain the Debye characteristic temperatures θ_D. θ_D increases progressively from 162^0K, at 15^0K to 186^0K and at 105^0K. Later on, more accurate determinations by Geballe and Giauque[16]. The results obtained for Debye Characteristic temperatures at different temperatures have been shown in Figure 2. The theoretical results are compared with the experimental values reported by Clusius and Harteck[15]. The theoretical results compare well with the experimental values available. The calculated and experimental specific heats of gold have been given in Table 4 for comparison.

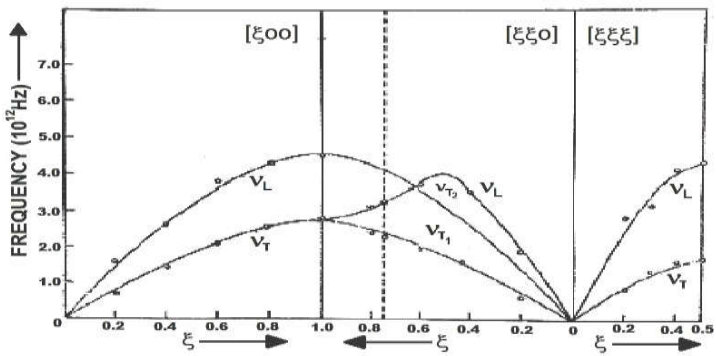

Figure 1. Phonon Dispersion Curves for Gold along Symmetry Directions. Experimental Points (0) are due to Lynn et al [13]

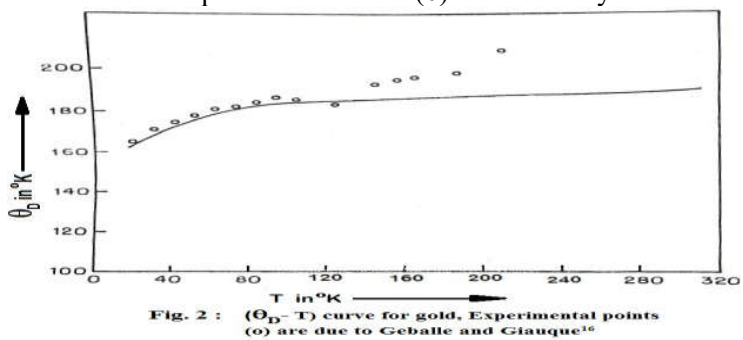

Figure 2. (Θ_D-T) Curve for Gold, Experimental Points (0) are due to Geballe and Giauque[16]

Table 4. Calculated and Experimental Specific Heats of Gold in Units of J $mol^{-1}K^{-1}$

Temperature T°K	Theoretical Specific Heat CV	Experimental Specific Heat CV -γe T
20		3.2008
30		7.3262
40	11.2964	11.1504
50	14.2256	14.1754
60	16.5268	16.4933
70	18.2004	18.1837
80	19.4556	19.4138
90	20.4598	20.3844
100	21.1292	21.1166
120	22.1334	22.0748
140	22.8028	22.6898
150	23.0120	22.9534
160	23.2212	23.1626
180	23.8070	23.4639
200	23.7651	23.6689

4. Discussion

Several theoretical calculations of phonon dispersion relations have been reported by various workers for gold. Those workers have applied different theoretical models for the lattice vibrations of metals including gold. Agarwal and Rathore[17], Thakur and Singh[14] have evaluated the phonon dispersion relations of gold with varied success. The present results of phonon dispersion relations of gold on a simple phenomenological model developed in the present work is comparable to other workers. Several attempts have been made earlier by different workers to compute theoretically the specific heat and Debye characteristic temperatures and their variations with temperatures. Bertolo and Shukla[18] have studied lattice dynamics, specific heat and Debye characteristic temperatures of gold. They have reasonable agreement with the experimental values. The present phenomenological model has been developed under harmonic approximation and does not take

account of anharmonicity of atoms which plays important role at high temperatures in thermal properties.

5. Conclusions

The present phenomenological model which considers two-body and three-body ion-ion interaction and also takes into account the ion-electron interactions explains satisfactorily the experimental phonon dispersion results, specific heat variation with temperature and Debye characteristic temperatures of gold. The present results compare well with available experimental and theoretical values reported by other workers for these properties.

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