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Lattice Dynamics of Silver

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ABSTRACT A phenomenological model for the lattice dynamics of silver 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 silver. 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 Screened Coulomb potential, phonon dispersion curve, specific heat, Debye characteristics temperature, phenomenological model, silver nanoparticles

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 silver.

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.

Recently some investigations on theoretical and experimental study of silver metal and its compounds have been reported on the properties related to silver nanoparticles, silver electroplating and anharmonic lattice vibrations. Theoretical and experimental studies were performed on the structure, optical properties and growth of nanostructures in silver phosphate by Botelho et al[5]. Mahdieh et al[6] reported the investigation of Ag, Al_2O_3 and TiO_2 nanoparticles effects as impurities in laser induced breakdown in distilled water. Pressure effect of the vibrational and thermodynamic properties of chalcopyrite-type compound $AgGaS_2$ were investigated by Yang et al[7] by a first principle method. A combined theoretical and experimental study for silver electroplating was made by Liu et al[8]. Very recently Fabara et al[9] applied the computational modeling of the interaction of silver nanoparticles with the lipid layer of the skin due to their unique optical, electrical and thermal

properties. Earlier Gordienko et al[10] reported the Ab initio calculations of the lattice dynamics of silver halides.

These recent investigations on theoretical and experimental study of silver metal and its compounds on properties related to silver nanoparticles, silver electroplating and anharmonic lattice vibrations motivated the present study of lattice dynamics of silver. 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 silver. The theoretical results have been compared with the available experimental data.

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[11] 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 element of the dynamical matrix corresponding to ion-electron interaction has been taken as reported by Mishra and Singh[12]. 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:

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

$$C_{12} = \frac{1}{2a}\left[-5\alpha_1 + \beta_1 - 4\alpha_2\right] + K_e \quad (8)$$

$$C_{44} = \frac{1}{2a}\left[3\alpha_1 + \beta_1 + 4\alpha_2 + 2\beta_3\right] \quad (9)$$

Where K_e is the bulk modulus of electron gas.

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

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

and

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

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 silver. The values of C_v at different temperatures are obtained from

$$C_v = \frac{3R}{3000}\sum_{\upsilon} E\left(\frac{h\upsilon}{KT}\right) g(\upsilon)$$

Where $g(\upsilon)$ the frequency distribution function for the metal, R is 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.

RESULTS

The Phonon dispersion curves along symmetry directions $[\xi 00],[\xi\xi 0]$ and $[\xi\xi\xi]$ of silver 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 curves along symmetry directions $[\xi 00],[\xi\xi 0]$ and $[\xi\xi\xi]$ have been presented in Figure 1. The results obtained were compared with the experimental data of Kamitakahara and Brockhoure[14]. The agreement of the present theoretical results with the experimental values is quite good.

The specific heats and Debye characteristic temperature of silver 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. 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 Meads et al[15]. The theoretical results compare well with the experimental values available. The calculated and experimental specific heats of silver have been given in Table 4 for comparison.

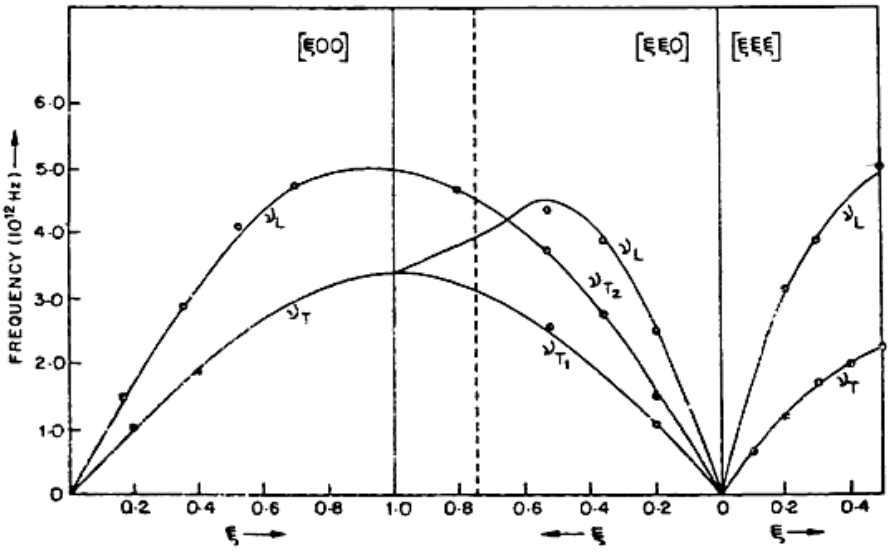

Figure 1: **Phonon dispersion curves for silver along symmetry directions. Experimental points (o) are due to Kamitakahara and Brockhouse[14]**

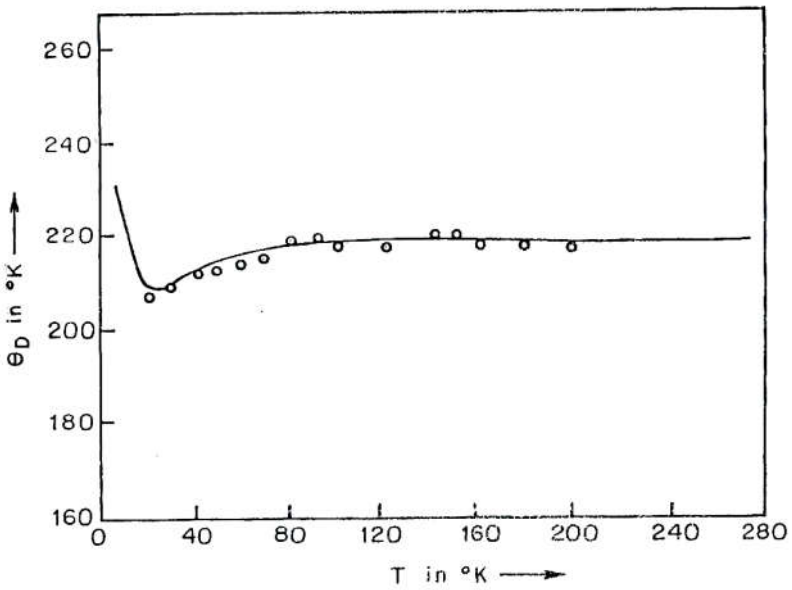

Figure 2: **(θ_D–T) curve for silver. Experimental points (o) are due to Meads et al[15]**

Table 1: Input data used for the determination of model parameters

Element	Elastic constants $10^{10}Nm^{-2}$			Reference for Elastic constants	Phonon frequencies 10^{12} s^{-1}		Reference for phonon frequencies
	C_{11}	C_{12}	C_{44}		ν_{LO}	ν_{TO}	
Silver	12.39	9.37	4.61	[13]	4.96	3.41	[14]

Table 2: Values of physical quantities used in the calculations

Element	Atomic radius	Lattice constant	Atomic mass	F. S. wave vector K_F	Screening multiplication constant σ
	10^{-10} m	10^{-10} m	10^{-27} kg	10^{10} m^{-1}	
Silver	1.595	2.040	179.060	1.203	0.353

Table 3: Values of model parameters and electron bulk modulus

Element	Force constants (Nm^{-1})					Bulk modulus K_e
	α_1	β_1	α_2	β_2	β_3	10^{10} Nm^{-2}
Silver	0.9444	14.1465	–0.428	–4.992	1.7745	5.18

Table 4: Calculated and experimental specific heats of silver in units of J $mol^{-1}K^{-1}$

Temperature T°K	Theoretical specific heat C_V	Experimental specific heat $C_V - \gamma_e T$
20	1.611	1.703
30	4.602	4.749
40	8.033	8.347
50	11.506	11.581
60	14.142	14.209
70	16.108	16.192
80	17.573	17.711
90	18.786	18.869
100	19.874	19.891
120	21.129	21.225
140	22.133	22.129
150	22.468	22.459
160	22.761	22.748
180	23.221	23.263
200	23.514	23.522

DISCUSSION

Several theoretical calculations of phonon dispersion relations have been reported by various workers for silver. Those workers have applied different theoretical models for the lattice vibrations of metals including silver. Agarwal and Rathore[16], Thakur and Singh[17] have evaluated the phonon dispersion relations of silver with varied success. The present results of phonon dispersion relations of silver on a simple phenomenological model developed in the present work are 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 silver. They have reasonable agreement with the experimental values. The present phenomenological model has been developed under harmonic approximation and does not take account of harmonicity of atoms which plays important role at high temperatures in thermal properties.

CONCLUSION

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 silver. The present results compare well with available experimental and theoretical values reported by other workers for these properties.

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