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Lattice Dynamics and Lattice Mechanical Properties of Gold and Silver Using Parameter Free Pseudopotential

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In the present communication, the local form of the pseudopotential is employed to study the lattice dynamics and some mechanical properties of the gold and silver lattice. We have treated pseudopotential parameters r_c and r_m as experimental radii to make present pseudopotential parameter-free and so our model does not require any adjustment of parameters. The computed results of phonon dispersion curves, Debye-Waller factor, mean square displacement, specific heat, isothermal bulk modulus and Debye temperature are reported for both metals. Our theoretical results are in accordance with experimental trend and overall good agreement is achieved when compared with available experimental findings.

Keywords: Pseudopotential, Noble metals, Debye-Waller factor.

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1. INTRODUCTION

Methods like first principles, local and non-local pseudopotential, are used to study the properties of noble metals [1-4]. To solve the problems on condensed matter physics, one can use the pseudopotential method initially as it is less complicated and less time-consuming. The second-order pseudopotential is mostly used for studying the interactions in a crystal with a cubic lattice structure. The evolution of local pseudopotential is considerable for simple metals while local pseudopotential for transition metals is not much evolved. Many pseudopotentials are developing with adjustable parameters [5-8]. The existence of d-band electrons complicates the behavior of transition metals, so for the theoretical explanation of many properties, *s-p* hybridization should be taken into account. Lattice dynamics can be calculated using reciprocal and real space vectors. Non-local pseudopotentials are good but are complicated, mathematically less transparent and computationally convoluted.

Among all the types of pseudopotentials, local pseudopotential is broadly used because it can be easily operated and extended to study properties at extreme conditions for metals with a complex electronic configuration like transition metals, rare earth metals, actinides and lanthanides [9-11]. Local pseudopotential is handy and can be operated well by simply adjusting the valency [12]. The literature survey suggests that the lattice mechanical properties require adjustable parameters. The main aim of the present work is to carry out computational work without adjusting the parameters like first principles method. In the present work, Kumar's local pseudopotential is taken for the aid of calculations of dynamical elastic constants, Debye Waller factor and mean square displacement for gold and silver [13].

In the current era, nanotechnology is growing in leaps and bounds where silver and gold play a vital role in development and research. Silver and gold are common components of nano-sols, nano-colloids, nanorods, nanotubes, and nanowires created using a range of physical and chemical methods. Because of their unique shape- and size-dependent optical characteristics, silver and gold nanoparticle-based colorimetric sensors provide promising prospects for the creation of efficient sensors [14]. Silver and gold nano cubes outperformed nano-spheres and nanowires in terms of antifungal activity against the test species [15]. Silver nanoparticles can be used to generate heat at the nano level. This has numerous emerging uses in photothermal imaging, photothermal therapy, and thermo-photovoltaics [16]. Although platinum-based medications akin to cisplatin are powerful metastatic tumor agents, they have infelicitous effects. There is, therefore, a desire for brand new drugs with an improved spectrum of effectiveness and lower toxicity. Complexes of copper, gold and silver are potential candidates to fulfil this need. An appreciable effort has conjointly been placed into interpreting the mechanisms of action of those complexes and optimizing their bioactivity through structural modification [17]. The nano dipole antenna is used to design and simulate THz communication using CST MICROWAVE STUDIO which is constructed using the noble metals silver and gold as the nanomaterials [18]. Metal-based medicines are utilized in the Indian medical systems, namely Ayurveda and Siddha where gold and silver-based medicines are the foremost popular. Gold and silver ashes are used to treat neuropsychiatric disorders [19]. Hence, looking at the importance of gold and silver, authors are motivated to investigate the lattice dynamical and lattice mechanical properties of these metals.

2. THEORY

We have used Kumar's local form of pseudopotential to investigate several lattice dynamic and lattice mechanical features for noble metals Ag and Au. The

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pseudopotential has the following form in q-space [13],

$$V_{ion}(r) = \frac{-Ze^2 r}{r_m r_c} \quad \text{for } 0 < r < r_c,$$
$$V_{ion}(r) = \frac{-Ze^2}{r_m} \quad \text{for } r_c < r < r_m, \qquad (1)$$
$$V_{ion}(r) = \frac{-Ze^2}{r_m} \quad \text{for } r_m < r.$$

where Z is the effective valency.

The present model potential does not require any adjustment of parameters. In order to present a parameter-free pseudopotential, we have considered r_c as ionic radii and r_m as atomic radii, and both are experimental radii taken from Ref. [20].

To obtain the vibrational frequency $\omega_{\vec{q},\lambda}$ for $\vec{q}$, λ mode, one essentially requires to diagonalize the dynamical matrix for different values of $\vec{q}$ [21]. The total dynamical matrix $D_{\alpha\beta}(q)$ is made up of two contributions. one columbic contribution $D^c_{\alpha\beta}(q)$ and second electronic contribution $D^E_{\alpha\beta}(q)$.

The Columbic contribution $D^c_{\alpha\beta}(q)$ is given by:

$$D^c_{\alpha\beta} = \frac{2}{M}\begin{bmatrix} \sum_Q G_1(|\vec{Q}+\vec{q}|)(\vec{Q}+\vec{q})_\alpha(\vec{Q}+\vec{q})_\beta - \\ \sum'_Q G_1(|\vec{Q}|)Q_\alpha Q_\beta + \\ \sum'_R\{\phi'_1(R)\delta_{\alpha\beta} + 2\phi''_1(R)R_\alpha R_\beta(1-\cos(\vec{q}\cdot\vec{R}))\} \end{bmatrix}. \qquad (2)$$

The expressions for $G_1(|\vec{\phi}|)$, $\phi_1(R)$ and $\phi''_1(R)$ are taken from Ref. [21].

The electronic contribution $D^E_{\alpha\beta}(q)$ is given by:

$$D^2_{\alpha\beta}(q) = \frac{2}{M}\begin{bmatrix} \sum_Q F(|\vec{Q}+\vec{q}|)(\vec{Q}+\vec{q})_\alpha(\vec{Q}+\vec{q})_\beta \\ -\sum'_Q F(|\vec{Q}|)\,Q_\alpha Q_\beta \end{bmatrix}, \qquad (3)$$

$$D^3_{\alpha\beta}(q) = \frac{6\Omega}{M}\sum_{\vec{Q}_1,\vec{Q}_2,\vec{Q}_3}\begin{bmatrix} (\vec{q}+\vec{Q}_1)_\alpha(\vec{q}+\vec{Q}_2)_\beta \times \Gamma^{(3)}(\vec{q}+\vec{Q}_1,-\vec{q}-\vec{Q}_2,\vec{Q}_3)\times \\ V_{ion}(|\vec{q}+\vec{Q}_1|)V_{ion}(-|\vec{q}+\vec{Q}_2|)V_{ion}(|\vec{Q}_3|)\times \\ \Delta(\vec{Q}_1-\vec{Q}_2+\vec{Q}_3) \end{bmatrix}. \qquad (4)$$

We have carried out the study of dynamical elastic constant in the long wavelength limit ($q \to 0$) using theoretical method described in Ref. [22].

We have adopted dynamic approach and calculated dynamical elastic constants C_{11}, C_{12}, C_{44} and bulk modulus B and compared with experimental results [21-23] and available theoretical results [26-30].

3. RESULTS AND DISCUSSION

The values of pseudopotential parameters, along with the input parameters used in the calculations, are presented in Table 1.

Table 1 – Input and pseudopotential parameters used in the calculation

Metal	Ω (a.u^3.)	Valency Z	Mass M [23] (a.m.u.)	Pseudopotential parameters [20]	
				r_c (a.u.)	r_m (a.u.)
Ag	115.1	1.3	107.88	2.1735	3.3075
Au	114.4	1.5	197	1.6065	3.3831

The computed curves of phonon dispersion for Ag are presented in Fig. 1. These results are compared with experimental results due to Kamitakahara and Brockhouse [24]. For Au computed results are shown in Fig. 2 and compared with experimental results due to Lynn et al. [25].

In both longitudinal and transverse modes, the agreement between experimental measurements and our estimated frequencies is excellent, particularly for Au. We would like to emphasize that the present version of pseudopotential is parameter-free and requires no phonon frequency modifications. To our knowledge, no other approaches for studying lattice dynamics utilizing local pseudopotential have been adopted.

Elastic constants relate with stress and strain which can be studied by using two different approaches first one is static and another one is the dynamic approach.

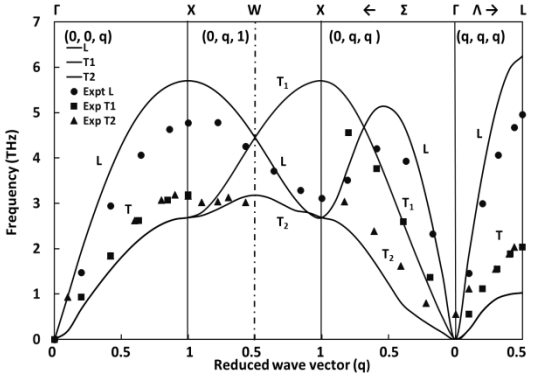

Fig. 1 – Phonon dispersion curves for Ag

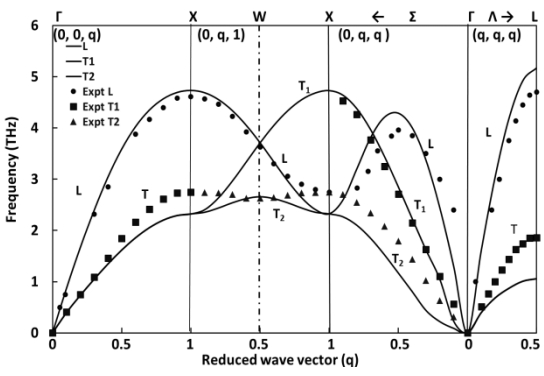

Fig. 2 – Phonon dispersion curves for Au

Table 2 – Dynamical Elastic Constants C_{11}, C_{12}, C_{44} and bulk modulus B for Ag and Au. All quantities are in [10^{12} dyne/cm^2]

		Present	Experimental	Other theoretical results
Ag	C_{11}	1.42	1.315 [23]	0.882 [26], 1.182 [27], 1.326 [28], 1.24 [29], 1.2695 [30]
	C_{12}	1.85	0.973 [23]	0.791 [26], 1.021 [27], 0.984 [28], 0.937 [29], 0.8849 [30]
	C_{44}	0.33	0.511 [23]	0.442 [26], 0.498 [27], 0.511 [28], 0.461 [29], 0.5050 [30]
	B	1.71	1.08 [23], 1.007 [21]	0.820 [26], 1.074 [27], 1.098 [28], 1.0131 [30]
Au	C_{11}	1.78	2.016 [23]	1.500 [26], 1.887 [27], 1.954 [28], 1.923 [29], 1.5824 [30]
	C_{12}	2.28	1.697 [23]	1.286 [26], 1.634 [27], 1.637 [28], 1.348 [29], 1.31 [30]
	C_{44}	0.424	0.454 [23]	0.703 [26], 0.484 [27], 0.445 [28], 0.438 [29], 0.3492 [30]
	B	2.11	1.732 [21]	1.357 [26], 1.718 [27], 1.098 [28], 1.4045 [30]

The computed results have a good agreement with experimental results for Au, the maximum deviation for dynamical elastic constants is 25 % in C_{12}. For Ag, the results vary by 7.3 % for C_{11} but values of C_{12} and C_{44} are not matching well with experimental values. Many studies have highlighted that in order to include core-core repulsions in noble metals, one must utilize the Born-Mayer type of potential for local as well as non-local pseudopotentials. The current computation is independent of parameter variations, and the potential itself includes *s*, *p*, and *d* hybridization. In this context, currently employed pseudopotential can be considered as the first principles pseudopotential.

Using the root sampling approach, we estimated the phonon density of states in the harmonic approximation. In order to do these calculations, a mesh of 64000 wavevectors was used in the first Brillouin zone. Using the calculated frequency distribution, the Debye-Waller factor (W_T) and mean square displacement ($\bar{U}^2$) is computed. The detailed equations can be found in [21]. The temperature variations of W_T and $\bar{U}^2$ along with the experimental results due to Peng et al. [31] are shown in Fig. 3 for Ag and Fig. 4 for Au respectively.

From the results, it can be clearly seen that the computed results are showing an experimental trend but not in quantitative agreement with the experimental results. One of the reasons for this disagreement is that in these computations three-body forces are not accounted for.

Thermodynamic properties carried out at different temperatures under ambient temperature have enhanced our understanding in different ways. Such studies grabbed the attention of many researchers particularly physicists and chemists as they discovered that there is a clear indication of the possibility of quantum effects at such temperatures Recently, superconductivity, propellant, cryogenics, including several additional technologies have risen low-temperature research to a great extent. Specific heat and other thermodynamic properties are very important in engineering, particularly when designing systems that require heat management. It also includes everything from refrigerating to heating and, nearly anything in electronics where heat waste management is important. In terms of frequency distribution, the specific heat C_P is computed using the following expression:

$$\frac{C_v}{3R} = \int_0^{\omega_{max}} \left[\frac{\left(\frac{\hbar\omega}{k_BT}\right)^2 \exp\left(\frac{\hbar\omega}{k_BT}\right)}{\left[\exp\left(\frac{\hbar\omega}{k_BT}\right)-1\right]^2}\right] g(\omega)d\omega. \quad (5)$$

The computed temperature variations of specific heat C_P compared with experimental data [21] are presented in Fig. 5 and Fig. 6 for Ag and Au, respectively.

It can be clearly seen that our theoretical results of specific heats are in excellent agreement with experimental data with a maximum deviation of 8 % for Ag and 6 % in the case of Au. We have also studied isothermal bulk modulus which is displayed in Fig. 7 for Ag and Fig. 8 in Au, respectively.

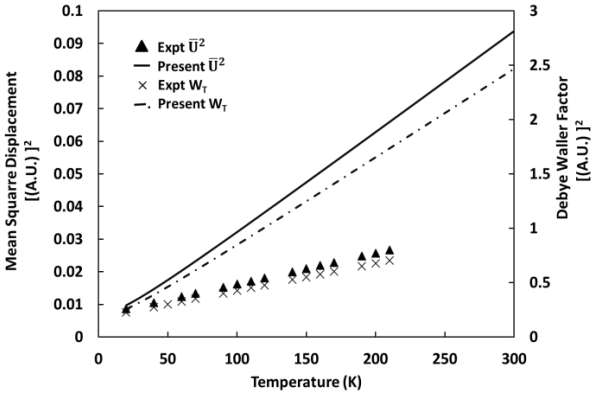

Fig. 3 – The temperature variations of W_T and $\bar{U}^2$ for Ag

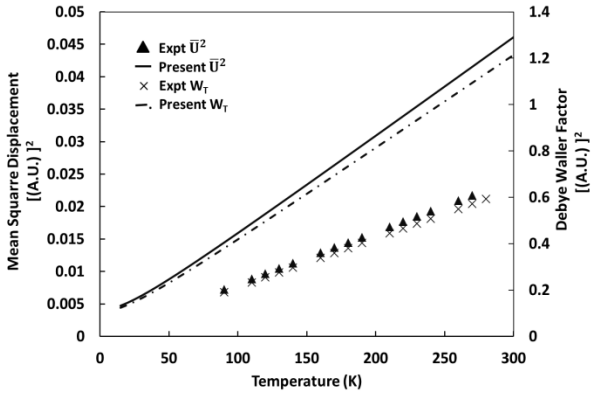

Fig. 4 – The temperature variations of W_T and $\bar{U}^2$ for Au

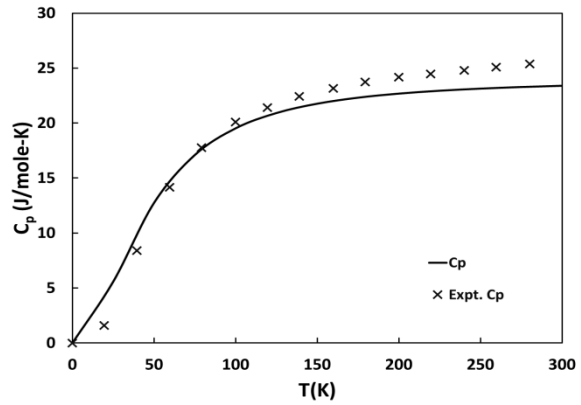

Fig. 5 – The temperature variations of C_p for Ag

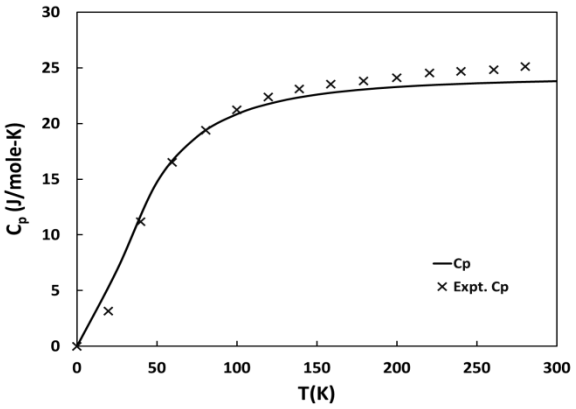

Fig. 6 – The temperature variations of C_p for Au

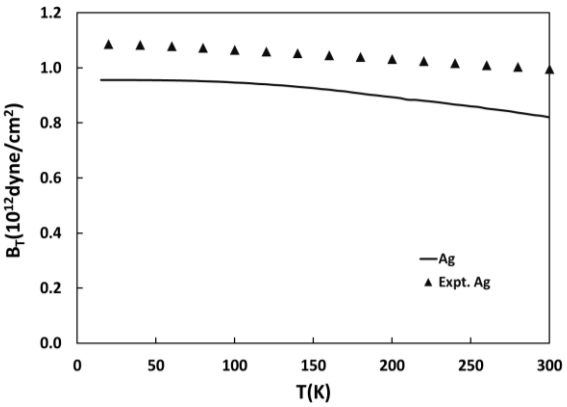

Fig. 7 – The temperature variations of B_T for Ag

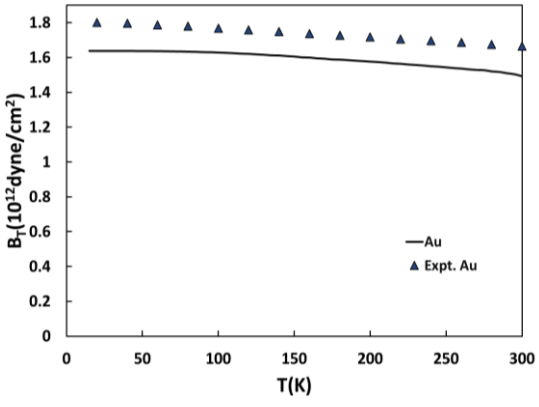

Fig. 8 – The temperature variations of B_T for Au

It is observed that the total presently calculated results of B_T for Ag and Au both are closely matching with experimental results but for Ag, the disagreement between computed data and experimental ones increases with temperature with a maximum deviation of 17 % whereas for Au it is 10 %. Another most important physical property in solid-state physics is Debye temperature as it correlates the elastic properties and thermodynamic properties such as phonon frequencies, specific heat, enthalpy, thermal expansion etc. The presence of the Debye temperature in so many aspects of condensed matter physics is sufficient proof for the significance of specific heat investigations. Debye temperatures for both studied metals up to 300 K are plotted and compared with experimental results [32-34] in Fig. 9 and Fig. 10.

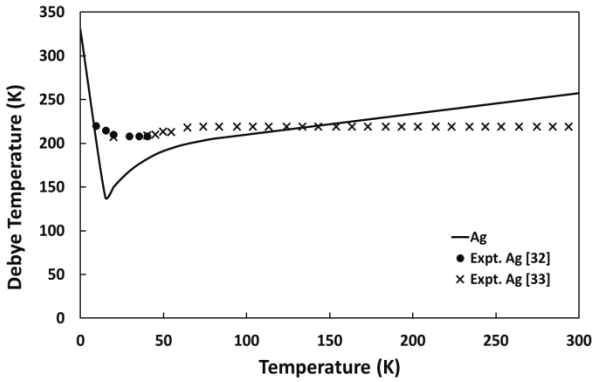

Fig. 9 – The temperature variations of θ_D for Ag

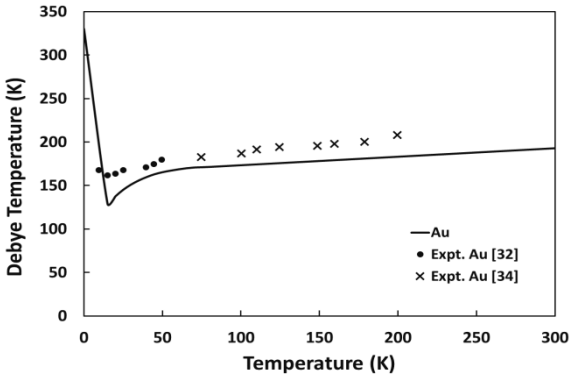

Fig. 10 – The temperature variations of θ_D for Au

Our results are in affirmation and overall good agreement with the experimental record is obtained. In case of Ag, the deviation between computed results and experimental results decreases as temperature increases but as temperature approaches to 300 K, the deviation increases again. For Au, present results are in excellent agreement with available experimental data.

4. CONCLUSIONS

From this study, we can conclude that Kumar's local form of pseudopotential can be used for the primary study of lattice dynamics and lattice mechanical properties of noble metals with our presently adopted approach of radii. This pseudopotential is equivalent to first principles

pseudopotential as no adjustment of parameters were considered. Better agreement between computed results from experimental ones in the case of the Debye-Waller factor and mean square displacement can be obtained if three-body forces are accounted for.

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Динаміка та механічні властивості решітки золота та срібла з використанням безпараметричного псевдопотенціалу

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У статті локальна форма псевдопотенціалу використовується для вивчення динаміки та деяких механічних властивостей решітки золота та срібла. Ми розглядали параметри псевдопотенціалу r_c та r_m як експериментальні радіуси, щоб зробити поточний псевдопотенціал безпараметричним, і тому наша модель не вимагала жодного коригування параметрів. Для обох металів наведено обчислені результати кривих дисперсії фононів, фактору Дебая-Воллера, середньоквадратичного зміщення, питомої теплоємності, ізотермічного об'ємного модуля та температури Дебая. Наші теоретичні результати відповідають експериментальним даним, і в цілому досягається гарне узгодження з доступними експериментальними результатами.

Ключові слова: Псевдопотенціал, Благородні метали, Фактор Дебая-Воллера.