LATTICE DYNAMICS OF NOBLE METALS

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The screened shell model proposed by Fielek has been applied in its simplified form to compute the phonon dispersion relations for lattice waves propagating along the three principal symmetry directions of silver and gold. The theoretical results are compared with the existing experimental data and an agreement reasonably satisfactory to warrant their publication has been achieved.

1. Introduction

It is a well-known fact that thermal vibrations play a dominant role in numerous physical phenomena which for their detailed explanation require a knowledge of the actual form of the vibrational spectrum. In spite of several attempts [1–8] to develop a more realistic model based on first principles and pseudopotential approach, the task is formidable even today. Therefore, the development of phenomenological models have received much attention in the last few years.

Some phenomenological models have been proposed by various workers to describe the lattice vibrations in metals. These models, however, do not give a good fit to the phonon dispersion curves of non simple metals such as Shukla [9] pointed out for noble and Hauteclar and Van Dingenen [10] for transition metals. The reason for this is believed to be that the outermost *d*-electrons are loosely bound to their respective nucleus. Hence the effect of outermost *d*-electrons cannot be ignored. Using this hypothesis Fielek [11] proposed a simple screened shell model and applied it successfully to the study of lattice waves dispersion in copper and nickel.

In the present paper, we report on the dispersion curves of silver and gold along three principal symmetry directions on the basis of Fielek model. The stimulus for this study is provided by the success of this model in the explanation of the gross features of the thermal properties of copper. The calculated results for siver and gold are presented along with the existing experimental data.

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2. General formulation

The secular equation determining the frequency ν of the normal mode vibrations may be represented as

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

where $\boldsymbol{q}$ is the phonon wave vector, M is the mass of the ion and I is a unit matrix of order three.

The expressions for two typical elements of the secular equation (1) are written below.

$$D_{ii}(\boldsymbol{q}) = D'_{ii}+\frac{K^2}{N}, \qquad D_{ij}(\boldsymbol{q}) = D'_{ij} \tag{2}$$

$$D'_{ii} = -2\alpha_1\{2-C_i(C_j+C_k)\}-4\alpha_2 S_i^2-K+AG(\boldsymbol{q}),$$

$$D'_{ij} = -2\alpha_1 S_i S_j, \tag{3}$$

where $C_i = \cos(aq_i)$, $S_i = \sin(aq_i)$. q_i is the i-th component of the phonon wave vector $\boldsymbol{q}$, $2a$ is the lattice parameter.

Further, one can easily determine N by applying the adiabatic approximation to the shell equation and then with the help of the determinant

$$|D''(\boldsymbol{q})-NI| = 0. \tag{4}$$

The typical elements of the above determinant are expressed as

$$D''_{ii} = 2S\{2-C_i(C_j+C_k)\}+K-A'G(\boldsymbol{q}), \qquad D''_{ij} = 2SS_iS_j. \tag{5}$$

Here the force constants α_1, α_2, S, A and A' are as defined by Fielek. The expressions for the remaining elements can be derived in cyclic order from equations (3) and (5).

TABLE I

Input data for the force constants

Metal	Elastic constants ($\times 10^{11}$ dyn cm^{-2})			Lattice constant	Zone boundary frequencies in [ζ00]$\times 10^{12}$ Hz	
	C_{11}	C_{12}	C_{44}	$2a$ (Å)	ν_L	ν_T
Silver	12.3990	9.3670	4.6120	4.080	4.95	3.43
Gold	19.2340	16.3140	4.1950	4.0780	4.61	2.75

TABLE II

Output values of the force constants (in units of 10^3 dyn cm^{-1})

Metal	α_1	α_2	K	S	A'
Silver	−23.9394	1.6116	33.9174	5.1224	43.9167
Gold	25.6872	1.2999	1233.2842	−42.7940	111.8203

The dynamical parameters of the theory can be connected with the elastic constants by taking the long wavelength limit and two zone boundary frequencies ν_L and ν_T in the [ζ00] direction. By solving Eq. (1) and taking $A = 0$ as considered by Fielek, we obtain

$$\alpha_1 + S = -2aC_{44}, \quad 2\alpha_2 = -a(C_{11} - C_{12} - C_{44}), \quad A' = (C_{12} - C_{44})2a^3k_c^2,$$

$$4\pi^2 M\nu_L^2 = -8\alpha_1 - K + \frac{K^2}{K + 8S - A'G(q)},$$

$$4\pi^2 M\nu_T^2 = -4\alpha_1 - K + \frac{K^2}{K + 4S - A'G(q)}. \tag{6}$$

The input data for the computation of these parameters are listed in Table I while the output values of the calculated force constants are given in Table II.

3. *Result and discussion*

The calculated values of the parameters have been used to investigate the nature of the phonon dispersion curves along the [ζ00], [ζζ0] and [ζζζ] directions of the two noble metals silver and gold. We have taken the experimental values of elastic constants obtained from the measurements of Neighbours and Alers [12] for these two noble metals. The resulting phonon dispersion curves along with the experimental points for silver of Kamitakahara and Brockhouse [13] and for gold of Lynn et al. [14] are plotted in Fig. 1

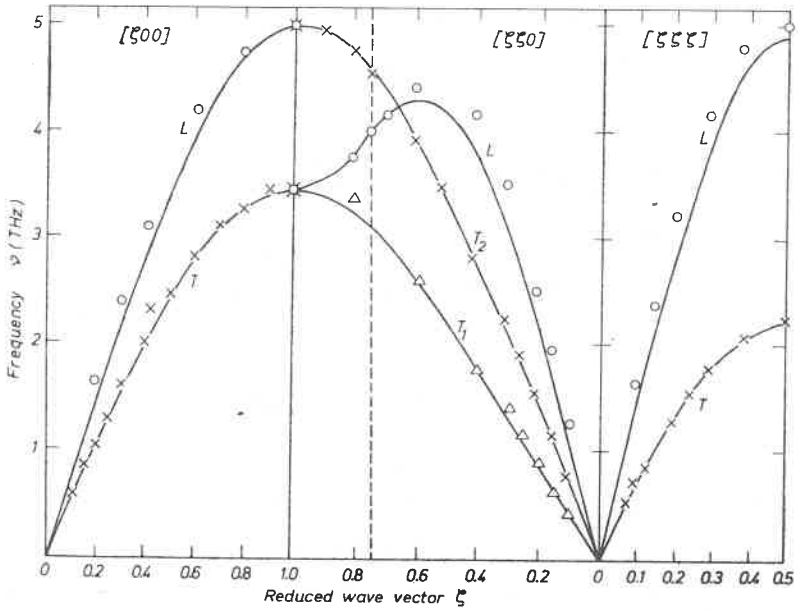

Fig. 1. Dispersion curves along the symmetry directions for silver, solid curves correspond to present calculations. Experimental points are indicated by ○, ×, △ (Kamitakahara and Brockhouse)

and Fig. 2, respectively. These figures show that there is an excellent agreement between theoretical and experimental measurements for all the transverse branches but that is not true for the curves of the longitudinal branches. The slight deviations from the measured values in the longitudinal branches may be due to

(a) neglect of contributions from the second neighbours of the *d*-shell;
(b) the form of the dielectric function and pseudopotential used;
(c) the assumption that $A = 0$.

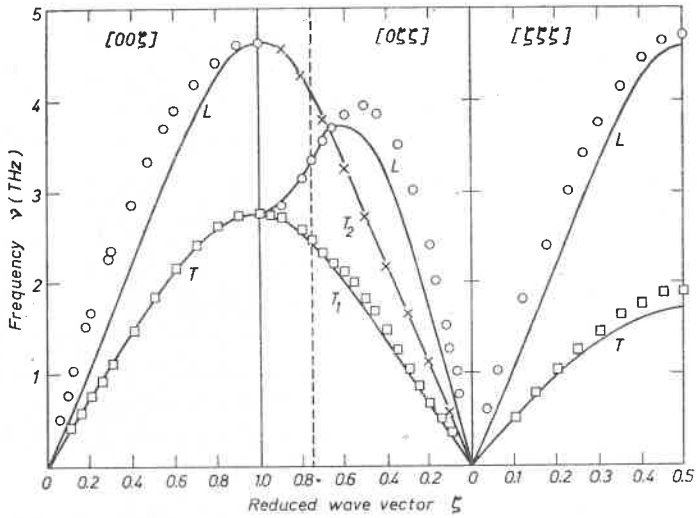

Fig. 2. Dispersion curves along the symmetry directions for gold, solid curves correspond to present calculations. Experimental points are indicated by ○, ×, △ (Lynn et al.)

As things stand it emerges from the present study that the lattice vibrations in noble metals could be explained satisfactorily with this simple model.

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