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Quasiharmonic lattice dynamics of noble metals

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To study the thermal expansion of fcc metals we propose an interatomic potential that considers both two- and three-body uncoupled forces that allows for the separate evaluation of both contributions. The aim was to develop a simple model that can explain a broad spectrum of lattice properties. This was satisfied by a model with only four independent parameters that are fitted to the experimental values of the second-order elastic constants and the Grüneisen function for $T \rightarrow \infty$. We calculate the dispersion curves, the second- and third-order elastic constants, and the temperature dependence of both the heat capacity and the Grüneisen function and compare with experimental data. We also analyze the contribution of each normal mode through its angular frequency and its Grüneisen parameter.

I. INTRODUCTION

To simulate the lattice properties of a metal requires knowledge of the effective interatomic potential. Its characterization from first principles is, at present, not possible; hence, a phenomenological approach will be very useful, particularly when one considers essentially anharmonic properties, such as the thermal expansion.

When we search through the literature about the models used to study the lattice properties of metals, one finds that many of the works consider only central forces, which cannot explain the observed violation of the Cauchy relations. Others works use the general force model,[1] which, owing to the greater number of parameters, is difficult to extend to consider also essentially anharmonic properties.

Recently, Zoli[2] and Zoli *et al.*[3] have used a model that includes three-body forces to calculate, for the noble metals, the phonon line shifts and the Grüneisen function for temperatures greater than 100 K. They have fitted the parameters of this model to the experimental dispersion curves and second- and third-order elastic constants (SOEC's and TOEC's). As the quasiharmonic approximation is essentially valid at low temperatures, we consider it very convenient to extend the calculation to this range. On the other hand this range has a particular physical interest because of the observed "anomalies" in both the heat capacity and the Grüneisen function. Moreover, compared with more complex systems the fcc metals are relatively simple ones. So, in order to allow an extension of the model to these last materials, we consider that it would be very useful not to include the dispersion curves in the fit of the parameters because, mainly, these data are not always available for other systems. Instead these data could be used as a further check of the developed model. A similar situation occurs with the use of the TOEC, or the SOEC pressure derivatives, but in addition the experimental error in these can be considerable. When available, the differences of reported values of the SOEC pressure derivatives from different authors make greatly difficult, as we will show later, the characterization of the anharmonic contribution to the total potential.

On the other hand, only in recent years have there been proposed other interaction potentials that consider many-body forces. For example, in the embedded atom method[4] the interaction is assumed to be the sum of two-body (repulsive) and n-body (cohesive) potentials. In this approximation the n-body potential is described through the embedding function which depends on the radial distribution of neighbors but not on their angular distribution. So this approach would not enable us to study the relative importance between central (two-body) and angular (three-body) forces. Moreover, this approach does not give (at least with the parametrization presently available) a good description of the dispersion curves[5] and then their extension to the study of also anharmonic properties is not immediate.

In the interstitial electron model,[6] the many-body interactions are indirectly taken into account by treating the valence electrons as classical particles localized in tetrahedral holes. Li and Goddard[6] parametrized this model with the experimental values of the SOEC's and frequencies of vibration at the point X in reciprocal space. Again, this model does not allow us to study the relative importance between two- and three-body forces and its extension to include also essentially anharmonic properties would involve a greater number of parameters, which could not be adequately determined from the experimental information available at present.

So, in this paper, we have two main objectives. First we are interested in the study of the relative importance between two- and three-body forces in the lattice dynamics of fcc metals. And, second, we wish to calculate the TOEC's and the temperature dependence of the Grüneisen function in order to consider also the evaluation of essentially anharmonic properties. The main idea of this work is to study the characteristics that the effective interaction potential should verify, in order to allow us the evaluation of a great number of lattice properties (both esentially harmonic and anharmonic ones). For this, we propose a simple interaction potential that considers two- and three-body uncoupled forces. This model is applied to the concrete case of fcc metals for which we calculate the dispersion curves, the second- and third-order elastic constants, and the temperature dependence of both the lattice heat capacity and the lattice contribution to the Grüneisen function for temperatures between 0 and 300 K. We analyze also the microscopic information the model gives.

II. DESCRIPTION OF THE MODEL

Here we propose an effective interatomic potential (Ψ) that can be expressed as the sum of two- (Φ) and three-body (X) uncoupled potentials. We consider the two-body potential of the form

$$\Phi = \frac{N}{2} \sum_{A} \phi(r_A), \tag{1}$$

where r_A is the distance between atom A and the one at the origin. The summation indicated in Eq. (1) must be carried out, in principle, over all atoms A of the crystal; however, here we consider the interactions only up to the second neighbors.

The three-body potential can be expressed as a function of the cosine of each angle subtended by each triad of atoms; with one of these fixed to the origin,

$$X = \frac{N}{2} {\sum_{AB}}' \chi[\cos(\theta_{AB})], \tag{2}$$

where θ_{AB} is the angle subtended by the bonds r_A and r_B. The prime in the summation indicates that terms in which two indices are equal must be omitted. The interaction potential associated with each angle (not each triad of atoms) can be developed as

$$\begin{aligned}\chi = {} & \chi(\cos\theta^0_{AB}) + \chi'(\cos\theta^0_{AB})\,\delta(\cos\theta_{AB}) \\ & + \tfrac{1}{2}\chi''(\cos\theta^0_{AB})\,[\delta(\cos\theta_{AB})]^2 \\ & + \tfrac{1}{6}\chi'''(\cos\theta^0_{AB})\,[\delta(\cos\theta_{AB})]^3,\end{aligned} \tag{3}$$

where θ^0_{AB} is the angle subtended by the atoms A, B, and the one at the origin when they are in their mean positions.

To develop the expressions for the pressure, the elastic constants, the dynamical matrix, and its strain derivative, it is useful to define the following quantities:

$$\alpha_A = \frac{\phi'(r^0_A)}{r^0_A}, \tag{4}$$

$$\beta_A = \phi''(r^0_A) - \alpha_A, \tag{5}$$

$$\delta_A = r^0_A\,\phi'''(r^0_A) - 3\beta_A, \tag{6}$$

where r^0_A indicates the distance between the atom at the origin and the atom A when both are in their mean positions. So we can characterize the interaction with the first neighbors given α_1, β_1, and δ_1, and with the second neighbors given α_2, β_2, and δ_2.

If we inspect the expression for the elastic constants, the dynamical matrix, and its strain derivative, we can see that the parameters $\chi'(\cos\theta^0_{AB})$ and $\chi''(\cos\theta^0_{AB})$ do not appear independently but through the combination

$$\zeta = \frac{\chi'(\cos\theta^0_{AB}) - \frac{2}{3}\chi''(\cos\theta^0_{AB})}{X^0_{AB}}, \tag{7}$$

where X_0 is half the lattice spacing. So, with this model, we can characterize the three-body forces by giving the parameters ζ and $\chi'''(\cos\theta^0_{AB})$ (for the fcc structure and considering only the common nearest-neighbor three-body interaction $\theta^0_{AB} = 60°$). However, the parameter χ''' appears only in the TOEC, not in the SOEC, neither in its pressure derivatives, nor the dynamical matrix, nor its pressure derivative. Moreover, the parameter χ''' appears in the TOEC expressions in such a way that the contribution owing to these terms verifies the third-order Cauchy relations. After a detailed examination of the experimental error in the determination of the TOEC, we concluded that the parameter χ''' is essentially indeterminate. So we chose $\chi''' = 0$; in other words we are neglecting the anharmonic contribution of the three-body forces. Fortunately this does not involve any further approximation in the calculation of the dispersion curves, the pressure derivatives of the SOEC, the temperature dependence of the heat capacity, or the Grüneisen function, which are the properties we wish to calculate.

III. RESULTS

A. Parametrization

In Table I we give the input data used to characterize the model. The given SOEC's correspond to the 0-K extrapolated values.[7,8] For the $T \to \infty$ limiting value of the Grüneisen function, γ_∞, we have used the $T = 298$ K values as reported by White and Collins[9] without any attempt to reanalyze the experimental data.

As we have mentioned the parameters of the present model would be α_1, α_2, β_1, β_2, δ_1, δ_2, and ζ, with δ_1 and δ_2 the anharmonic ones. However, in this work we neglect α_1, α_2, and δ_2. We could consider the parameters α_1 and α_2 by using in the fitting a frequency of vibration of the experimental dispersion curves and the stability condition, but we do not do this because the properties we wish to calculate have shown to be relatively insensitive to these parameters (which are approximately two

TABLE I. Input data used to parametrize the model. The C_{ij} are in 10^{11} N/m^2 and X_0 in 10^{-10} m. γ_∞ is dimensionless.

Metal	X_0	C_{11}	C_{12}	C_{44}	γ_∞
Cu	1.805	1.762	1.249	0.818	1.98
Ag	2.045	1.315	0.973	0.511	2.38
Au	2.040	2.016	1.697	0.454	2.96

TABLE II. $\partial\gamma_0^l/\partial C'_{ij}$ calculated with the elastic continuum model and the experimental SOEC's.

	$\partial\gamma_0^l/\partial C'_{11}$	$\partial\gamma_0^l/\partial C'_{12}$	$\partial\gamma_0^l/\partial C'_{44}$
Cu	-0.29	+0.70	+1.21
Ag	-0.59	-0.67	-1.19
Au	-0.10	+0.55	+1.08

orders of magnitude smaller than the corresponding β's). We discard δ_2; i.e., we restrict the anharmonic interaction to first neighbors, because we wish to use only one (measured with enough precision) experimental property in the fitting. The quality of the obtained results shows the validity of this assumption.

Now it is convenient to discuss why we have used only the SOEC's and γ_∞ to parametrize our model. First we emphasize that we wish to develop a model with its corresponding parametrization to calculate a broad spectrum of lattice properties and for several metallic systems. So, although the dispersion curves are available for the noble metals, this information is not the case for other metals. The experimental dispersion curves will be used, then, to test the model. On the other hand several authors[3] have used the TOEC's or the pressure derivatives of the SOEC's to parametrize their models. However, this method does not assure us good values of γ_0^l (i.e., the $T \to 0$ K limiting value of the Grüneisen function) owing to the error in the experimental values of the C'_{ij}. Indeed, with the elastic continuum model (valid for $T \to 0$ K) we can calculate the partial derivatives of γ_0^l with respect to the C'_{ij}, giving the values listed in Table II. For this we must mention here that γ_0^l is (within the elastic continuum model) a linear function of the C'_{ij}, and so its values are not necessary to calculate $\partial\gamma_0^l/\partial C'_{i,j}$. Then, from the differences in the experimental values of the SOEC pressure derivatives reported by different authors (Table III), we can estimate roughly that the experimental uncertainty in these are not less than ~ 5%. Then we estimate the uncertainty in γ_0^l as $\Delta\gamma_0^l \sim \partial\gamma_0^l/\partial C'_{11}\,\Delta C_{11} + \partial\gamma_0^l/\partial C'_{12}\,\Delta C_{12} + \partial\gamma_0^l/\partial C'_{44}\,\Delta C_{44}$ resulting in about 14%, 17%, and 25% for copper, silver, and gold, respectively. This $\Delta\gamma_0^l$ is greater than that obtained from thermal data.[9] For ionic crystals it is usual to calculate γ_0^l from the C'_{ij} ; however, in these systems the last problem is not present because the $\partial\gamma_0^l/\partial C'_{ij}$'s are one order of magnitude smaller approximately.

B. Elastic constants

Once the model was parametrized we calculated the SOEC pressure derivatives and the TOEC's given in Tables III and IV, respectively. As a measurement of the absolute uncertainty in the experimental C'_{ij} we can take the differences between the values reported by Hiki and Granato[11] and Daniels and Smith,[10] resulting in about 10%, 30%, and 20% for Cu, Ag, and Au, respectively. For the uncertainty in the experimental TOEC, we expect a value still greater because their measurement requires more difficult conditions. With this consideration we can see that the agreement between experimental and theoretical values is satisfactory.

C. Dispersion curves

As we have mentioned, we computed the dispersion curves along the most symmetrical directions of reciprocal space. These are given in Fig. 1 together with the experimental data as measured by neutron diffraction. The maximum difference occurs at the point (100) of longitudinal branches being approximately 14% for Cu. If we

TABLE III. Experimental (by different authors) and theoretical (with the present model) SOEC pressure derivatives (dimensionless).

		Cu	Ag	Au
$\frac{\partial C_{11}}{\partial P}$	Theor.	6.04	6.20	5.26
	Expt.[a]	5.91	5.12	5.72
	Expt.[b]	6.36	7.03	7.01
	Expt.[c]		6.79	
$\frac{\partial C_{12}}{\partial P}$	Theor.	4.70	4.88	4.62
	Expt.[a]	5.03	3.61	4.96
	Expt.[b]	5.20	5.75	6.14
	Expt.[c]		5.48	
$\frac{\partial C_{44}}{\partial P}$	Theor.	2.40	2.45	1.93
	Expt.[a]	2.63	3.04	1.52
	Expt.[b]	2.35	2.31	1.79
	Expt.[c]		2.32	

[a] Reference 10.

[b] Reference 11.

[c] Reference 12.

TABLE IV. Experimental (with the reported error) and theoretical (with the present model) TOEC in 10^{11} N/m$_2$.

	Cu		Ag		Au	
	Expt.[a]	Theor.	Expt.[a]	Theor.	Expt.[a]	Theor.
C_{111}	-12.71±0.22	-14.87	-8.43±0.37	-11.31	-17.29±0.21	-15.05
C_{112}	-8.14±0.09	-8.44	-5.29±0.18	-6.73	-9.22±0.12	-10.43
C_{123}	-0.50±0.18	-0.14	+1.89±0.37	-0.15	-2.33±0.49	-0.41
C_{144}	-0.03±0.09	+0.43	+0.56±0.26	+0.46	-0.13±0.32	+1.24
C_{166}	-7.80±0.05	-7.87	-6.37±0.13	-6.11	-6.48±0.17	-8.77
C_{456}	-0.95±0.87	+0.72	+0.83±0.08	+0.77	-0.12±0.16	+2.07

[a]Reference 11.

consider the small number of parameters used and the relative simplicity of the model, we can see the agreement as good. Anyway, the agreement will be sufficient to calculate thermodynamic properties, such as the specific heat, which are slightly dependent on the frequency spectrum.

D. Heat capacity

The lattice contribution to the specific heat was calculated previously by several authors[1,13,14] with good agreement with the values obtained from experimental data. Here, we report our calculated values to prove the present model, which contains a smaller number of parameters than previous ones (the present model, 4 independent parameters; Lynn, Smith, and Nicklow,[1] 14 parameters; Miller and Brockhouse,[13] 12 parameters; Kamitakahara and Brockhouse,[14] 22 parameters). We have calculated C_v from experimental data, using the thermodynamical relation

$$C_p = C_v\,(1+\beta\gamma T), \tag{8}$$

where β is the volumetric coefficient of thermal expansion and γ is the Grüneisen function, defined by $\gamma = \beta V B_S / C_v$. V is the molar volume and B_S the adiabatic bulk modulus. As sources of experimental data we have

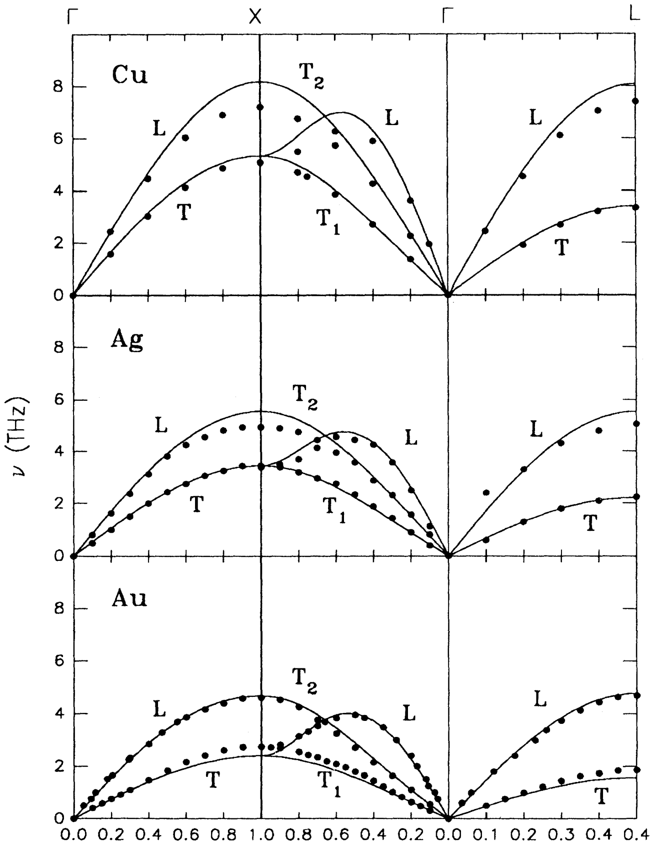

FIG. 1. Dispersion curves of copper, silver, and gold, according to the present model (solid line) and from experimental data (Refs. 13, 14, and 1) (points).

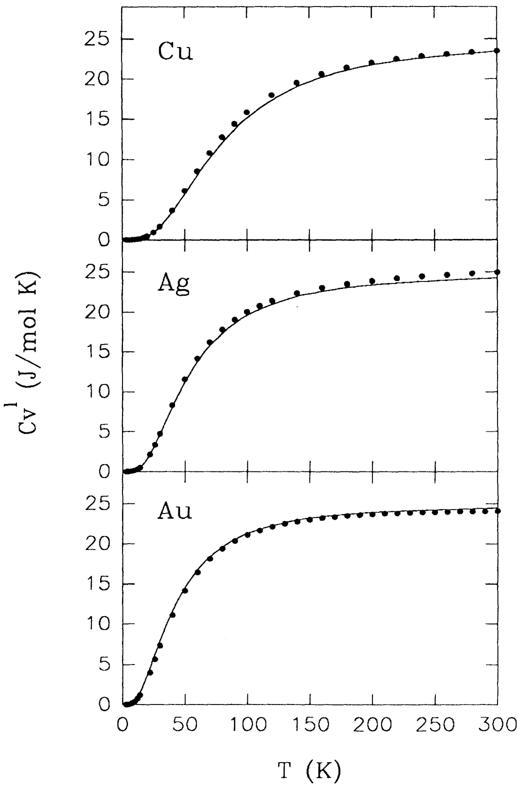

FIG. 2. C_v vs T curves calculated both from experimental data (points) and with the present model (solid line).

used the works of Martin[16,17] for the specific heat, White and Collins[9] for the thermal expansion, and Overton and Gaffney[7] and Neighbours and Alers[8] for the bulk modulus. In Fig. 2 we show the $C_v(T)$ curves calculated both theoretically and from experimental data, which show a good agreement.

E. Thermal Expansion

According to the quasiharmonic approximation, the Grüneisen function, at each temperature, can be evaluated as

$$\gamma(T) = \frac{\sum_{j=1}^{3N-6} \gamma_j(T)\, C_{v_j}}{\sum_{j=1}^{3N-6} C_{v_j}}, \tag{9}$$

where

$$C_{v_j} = k\left(\frac{h\nu_j}{kT}\right)^2 \frac{\exp h\nu_j/kT}{(\exp h\nu_j/kT - 1)^2} \tag{10}$$

and

$$\gamma_j = -\frac{\partial \ln \nu_j}{\partial \ln V} \tag{11}$$

are the Einstein specific heat and the Grüneisen parameter, both of the jth "normal" mode (N, the number of atoms of the crystal).

Figure 3 shows the temperature dependence of the lattice contribution to the Grüneisen function for the three metals considered in this work. For copper and silver there exists a very good agreement between the $\gamma^l(T)$ calculated with the present model and from experimental data for temperatures greater than ~ 20 K. For lower temperatures the theoretical curves pass through the very scattered "experimental" points but below its mean. For gold there is a reasonable agreement for temperatures between 70 and 300 K; for temperatures below 70 K the agreement is not very good with a maximum difference of about 2% at $T \sim 25$ K.

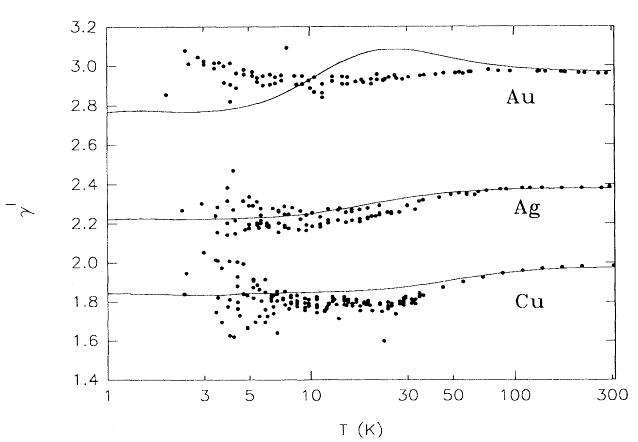

FIG. 3. Lattice contribution to the Grüneisen function calculated with the present model (solid line) and from experimental data Ref. 9 (points).

TABLE V. The 0-K limiting value of the Grüneisen function calculated (a) with the present model, (b) with experimental SOEC pressure derivatives, and (c) from experimental thermal expansion data.

	γ_0^l					
	(a)		(b)		(c)	
Cu	1.84	1.67[a]	1.73[b]		1.67[d]	1.78[e]
Ag	2.22	2.64[a]	2.14[b]	2.16[c]	2.29[d]	2.23[e]
Au	2.77	2.47[a]	2.91[b]		2.96[d]	2.94[e]

[a] Reference 11.

[b] Reference 10.

[c] Reference 12.

[d] Reference 9.

[e] Reference 18.

At very low temperatures the long wave phonons predominate and, in the $T \rightarrow 0$ K limit we can use the elastic continuum model to calculate γ_0^l, using the theoretical SOEC pressure derivatives; the results are given in Table V together with the values calculated using the experimental C'_{ij} and those obtained from thermal data. These γ_0^l can be also calculated as the limiting of $\gamma^l(T)$ for $T \rightarrow 0$ K in agreement with Eq. (9). However, this independent calculation is a test of the adequate evaluation of $\gamma^l(T)$ at very low temperatures which is the zone where the integration mesh in reciprocal space must be fine enough.

F. Microscopic information

The parameters β_1 that characterize the nearest-neighbor "harmonic" [see Eq. (5)] two-body potential and the parameters ζ that describe the common nearest-neighbor three-body forces, within the present model, are given in Table VI. As we can see, there exists a clear trend in the absolute and relative contribution of the three-body forces. Prakash and Upadhyaya[15] have used an explicit many-body potential to take into account the three-body forces. However, they have not found a clear trend in the relative importance of these forces possibly because the many-body potential they considered coupled the two- and three-body forces and their separation is difficult.

G. Grüneisen rule

According to the Grüneisen rule all the "normal" modes have the same Grüneisen parameter [Eq. (11)], leading to a function $\gamma^l(T)$ [Eq. (9)] independent of temperature. To study the validity of this rule we define

TABLE VI. Parameters β_1 and ζ of the present model.

Metal	β_1	ζ	β_1/ζ
Cu	39.90	-3.46	-11.53
Ag	33.50	-4.20	-7.98
Au	52.33	-11.27	-4.64

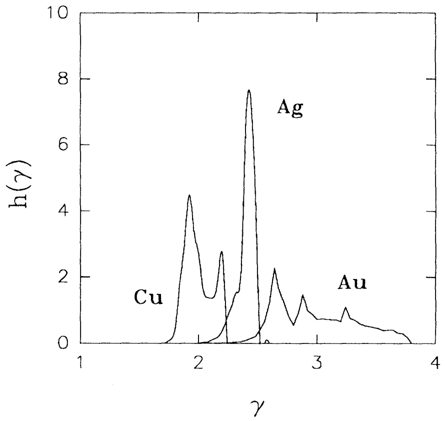

FIG. 4. Grüneisen parameter distribution function calculated with the present model.

the Grüneisen parameter distribution function $h(\gamma)$ such that $h(\gamma)\ d\gamma$ represents the relative number of "normal" modes with the Grüneisen parameter between γ and $\gamma + d\gamma$. In Fig. 4 we give the $h(\gamma)$ function calculated with the present model.

From a microscopic point of view, the Grüneisen rule requires that γ_j be constant. As we can see from Fig. 4 this is approximately obeyed for silver, to a lesser degree for copper, and very poorly for gold. On the other hand, from a macroscopical point of view, the Grüneisen rule requires that $\gamma^l(T)$ be constant. As a measurement of the fulfillment of this, we can use the differences $\gamma^l_\infty - \gamma^l_0$, which are 0.27, 0.26, and 0.12 for Cu, Ag, and Au, respectively. These differences represent changes in $\gamma^l(T)$ for T between 0 and 300 K of $\sim$ 13%, 11%, and 4%, respectively. So we can conclude that the Grüneisen rule is approximately obeyed by the three metals and particularly in a good degree by gold.

Therefore gold shows the interesting behavior that it fulfills $\gamma^l(T) = \text{const}$ to a good degree, but with a broad spectrum of the Grüneisen parameter. These two aspects are, of course, not incompatible and the fact that $\gamma^l(T)$ is constant is a consequence of an adequate weighting of the γ_j's by their corresponding C_{v_j}'s [Eq. (9)].

IV. CONCLUSIONS

We have proposed an interaction potential that considers both two- and three-body uncoupled forces and given a scheme of parametrization in which the four independent parameters of the model were fitted with the experimental values of the second-order elastic constants and the Grüneisen function for $T \to \infty$. The selection of this experimental data to characterize the model is an important feature of this work because this approach would allow us to study other systems in which more experimental information is scarcely available.

With this model we have calculated a broad spectrum of both essentially harmonic and anharmonic properties, dispersion curves, specific heat, second-order elastic constants, and Grüneisen function for copper, silver, and gold, obtaining, in all cases, a reasonable agreement with experimental data.

We have also studied the importance of three-body forces, showing the increasing importance of these in the series Cu-Ag-Au. In all cases the parameter ζ that characterizes the three-body forces is negative, suggesting that these interactions are essentially repulsive.

With this model we have shown that the fulfillment of the Grüneisen rule [$\gamma^l(T)$ constant] is in silver a consequence of a narrow Grüneisen parameter distribution function and in gold due to an adequate weight of the different γ_j. In copper the two effects together give a $\gamma^l(T) \sim \text{const}$.

We wish to emphasize that the aim of this work was to develop a simple model, with its corresponding scheme of parametrization, which allows us to calculate a broad spectrum of lattice properties. To test the model we have applied our approach to the noble metals because for these there are enough experimental data with which to compare.

At present we are applying our approach to study systematically all fcc metals for which there are less experimental data and expect in the future to extend the calculation to other structures.

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