Quasi-harmonic thermoelasticity of palladium, platinum, copper, and gold from first principles

Cristiano Malica and Andrea Dal Corso

International School for Advanced Studies (SISSA), Via Bonomea 265, 34136 Trieste, Italy
CNR-IOM, Via Bonomea 265, 34136 Trieste, Italy

E-mail: cmalica@sissa.it

Received 3 May 2021, revised 18 August 2021
Accepted for publication 23 August 2021
Published 8 September 2021

Abstract
We calculate the temperature-dependent elastic constants (ECs) of palladium, platinum, copper and gold within the quasi-harmonic approximation using a first-principles approach and evaluating numerically the second derivatives of the Helmholtz free-energy with respect to strain at the minimum of the free-energy itself. We find an overall good agreement with the experimental data although the anomalies of palladium and platinum reported at room temperature are not reproduced. The contribution of electronic excitations is also investigated: we find that it is non-negligible for the $C_{44}$ ECs of palladium and platinum while it is irrelevant in the other cases. Its effect is not sufficient to explain the details of the anomalies found by experiments, not even when, in the case of platinum, we take into account the electron–phonon interaction. Lastly, the effect of the exchange and correlation functional is addressed and it is found that it is important at $T = 0$ K, while all functionals give similar temperature dependencies.

Keywords: thermoelasticity, elasticity, electronic structure, mechanical & acoustical properties, phonons

Supplementary material for this article is available online
(Some figures may appear in colour only in the online journal)

1. Introduction
The vibrational and thermodynamic properties of transition and noble metals and of their alloys are key ingredients to understand many industrial and technological processes [1–3]. Moreover, the comprehension of these properties for elemental metals is a fundamental prerequisite for the rational design of materials. In addition to the extensive experimental investigations [4], the prediction of thermodynamic properties via density functional theory (DFT) [5, 6] has been among the primary goals of first-principles studies for many years (see for instance references [7, 8] and references therein).

In this context, the thermo_pw [9] code has been designed to compute efficiently, among other things, the thermodynamic properties of solids. Previous applications include the phonon dispersions, the thermal expansions, and the heat capacities of the hexagonal close-packed (hcp) metals rhenium, technetium [10], ruthenium, and osmium [11] and the anharmonic contributions to the mean square atomic displacements within the quasi-harmonic approximation (QHA) of silicon, ruthenium, magnesium, and cadmium [12].

Elastic constants (ECs) are other crucial quantities for crystal thermodynamics: they determine the crystal stability, thermal stresses, and sound velocities. For several decades DFT has provided ECs of solids, often within 10% from the experiment. However calculations have been usually limited to $T = 0$ K since the introduction of quantum and temperature
effects require a significant computational effort. As a result, there are now numerous theoretical ECs data at $T = 0$ K [13–15], but much less at finite temperatures. Some calculations do exist, but many of them are limited to the quasi-static approximation (QSA) where the temperature dependent elastic constants (TDECs) are calculated as second derivatives of the total energy with respect to strain (as at $T = 0$ K) at the minimum of the Helmholtz free-energy so accounting only for the effect of thermal expansion on the ECs. Only in a few papers the complete QHA method was applied (see, for example, references [16, 17]). Other calculations make use of the ab initio molecular dynamics method that, however, focus mainly on the high temperature behavior where quantum effects can be neglected [18].

The thermo_pw code can compute the ECs at $T = 0$ K (see for instance [19] and references therein) and, recently, the implementation was extended to the calculation of the quasi-harmonic TDECs as second derivatives of the Helmholtz free-energy with respect to strain [20]. So far, applications include the TDECs of silicon, aluminum, silver [20], and boron arsenide [21].

In this work, we apply this approach to other four paradigmatic face-centered cubic (fcc) transition and noble metals: palladium, platinum, copper, and gold. The first two elements, palladium and platinum, present anomalies in the experimental TDECs that are not well understood, while the latter two are more regular. Already after the early measurements on palladium and platinum some models were put forward to explain the anomalous temperature dependence of their ECs [22–25] and recently a computational DFT study has supported this interpretation [26]. These studies pointed out that the TDECs of palladium and platinum are anomalous due to the partially filled $d$ bands whose electrons contribute substantially to the free-energy. This theoretical study focused on the electronic contribution to the TDECs while the phonon contribution was accounted for within the QSA. Another theoretical study within the QSA, instead, finds a conventional temperature dependence for all the ECs of palladium, even considering the electronic thermal excitations [27].

Here we extend the previous QHA implementation in order to include the effects of the electronic excitations on the TDECs and compare the electronic and vibrational contributions. We find that the electronic contribution, although smaller than the vibrational one, is relevant for the temperature dependence of the $C_{44}$ ECs of palladium and platinum, where it improves the comparison with experiment, but it is not sufficient to reproduce in detail the anomalies. On the contrary, in copper and gold, whose $d$ shells are completely filled, the electronic contribution to the TDECs is negligible.

Focusing on platinum we investigate also another possible source of anomalous behavior. Actually electronic excitations might change the phonon frequencies especially at high temperatures, so we calculate the effect of this change on the TDECs. We find no substantial contribution, not even at the highest studied temperature of $T = 1000$ K.

Finally, since so far the effect of the exchange and correlation functionals on the TDECs has not been addressed in detail, we do also a systematic comparison between the local density approximation (LDA) and the generalized gradient approximation (GGA), taking the available experimental data as a reference. We find that all functionals give similar softening of the ECs with temperature, hence the functional that matches better the experimental ECs at $T = 0$ K turns out to be also the one that matches better the TDECs.

2. Theory

The QHA approach to the TDECs is detailed in the recent works [20, 21]: in this section we limit ourselves to a summary of the most important formulas in order to make the paper self-contained and discuss how we have introduced the electronic excitations in the calculation.

The isothermal ECs are obtained from the derivatives of the Helmholtz free-energy $F$ with respect to strain $\epsilon$:

$$C^T_{ijkl} = \frac{1}{\Omega} \left( \frac{\partial^2 F}{\partial \epsilon_i \partial \epsilon_j} \right)_{\epsilon = 0},$$

where $\Omega$ is the unit cell volume.

From the previous equation the free-energy $F$ contains a term quadratic in the strains:

$$F = \frac{\Omega}{2} \sum_{ijkl} \epsilon_{ij} \tilde{C}_{ijkl} \epsilon_{kl}.$$  

(2)

In cubic solids there are three independent ECs, $C_{1111}$, $C_{1122}$ and $C_{2323}$ which, for symmetry reasons [28] are usually written in Voigt’s notation as $C_{11}$, $C_{12}$ and $C_{44}$, respectively. We compute them using the deformations:

$$\epsilon_A = \begin{pmatrix} \epsilon_1 & 0 & 0 \\ 0 & \epsilon_1 & 0 \\ 0 & 0 & \epsilon_1 \end{pmatrix}, \quad \epsilon_E = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \epsilon_3 \end{pmatrix},$$

$$\epsilon_F = \begin{pmatrix} 0 & \epsilon_4 & \epsilon_4 \\ \epsilon_4 & 0 & \epsilon_4 \\ \epsilon_4 & \epsilon_4 & 0 \end{pmatrix}.$$  

(3)

The strain $\epsilon_A$ does not change the shape of the cubic cell, while $\epsilon_E$ transforms it into a tetragonal cell and $\epsilon_F$ into a rhombohedral cell. None of them conserves the volume of the cell.

As we are interested in the ECs obtained from the stress-strain relationship ($C^T_{ijkl}$ without $\tilde{\text{C}}$), when the system is under a pressure $p$, we correct the $C^T_{ijkl}$ [29]:

$$C^T_{ijkl} = \tilde{C}^T_{ijkl} + \frac{1}{2p} \left( 2\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} \right).$$

(4)

The Helmholtz free-energy of equation (2) is obtained as the sum of the DFT total energy $U$, the vibrational and the electronic free energies $F = U + F_{\text{vib}} + F_{\text{el}}$. The vibrational
free-energy is given by:

\[ F_{\text{vib}}(\varepsilon, T) = \frac{1}{2N} \sum_{q\eta} \hbar \omega_{\eta}(q, \varepsilon) + \frac{k_B T}{N} \sum_{q\eta} \ln \left[ 1 - \exp \left( -\frac{\hbar \omega_{\eta}(q, \varepsilon)}{k_B T} \right) \right], \]  

(5)

where \( N \) is the number of cells in the crystal, \( \omega_{\eta}(q, \varepsilon) \) is the phonon angular frequency of the mode \( \eta \) with wave-vector \( q \) computed in the system with a strain \( \varepsilon \). The \( \omega_{\eta}(q, \varepsilon) \) are computed by density functional perturbation theory (DFPT) [30] on a coarse \( q \)-point mesh and Fourier interpolated on a thicker mesh to perform the Brillouin zone summation.

In order to account for the thermal electronic excitations [31], one could use the Mermin’s finite temperature extension to DFT [32]. In this method, one minimizes the free-energy \( U - TS_\alpha \) where both \( U \) and the electronic entropy \( S_\alpha \) are calculated using the Fermi–Dirac occupations at a given fixed temperature \( T \). The method is accurate but needs a self-consistent calculation for each temperature. In order to evaluate the electronic free-energy for many temperatures we compute the total energy \( U \) with a Methfessel–Paxton smearing [33] and a broadening corresponding to the given temperature. Hence, the angular frequency \( \hbar \omega_{\eta}(q, \varepsilon) \) of equation (5) are replaced with the temperature dependent \( \hbar \omega_{\eta}(q, \varepsilon, T_{\text{FD}}) \), giving a correction to the Helmholtz free-energy. In this case the electronic excitations contribution is already included in the DFT total energy \( U \), via the Mermin’s functional, and it is not necessary to add it separately. We use this approach in platinum at enough large temperatures in order to clearly identify the effect, in particular at the temperatures \( T_{\text{FD}} = 800 \, \text{K} \) and \( T_{\text{FD}} = 1000 \, \text{K} \) and compare with the former method.

3. Computational parameters

The calculations presented in this work were carried out using DFT as implemented in the Quantum ESPRESSO package [44, 45]. For the calculations of ECs at \( T = 0 \, \text{K} \) and for all materials, the exchange and correlation functional was approximated by the LDA [46], the GGA of Perdew, Burke and Ernzerhof (PBE) [47] and its modification for dense packed solids (GGA–PBEsol) [48]. For the TDECs we use LDA and GGA–PBEsol for all metals and for copper we also use the GGA–PBE functional (which, in this case, gives the best agreement with the experimental \( T = 0 \, \text{K} \) ECs). We employ the projector augmented wave (PAW) method and a plane waves basis set with pseudopotentials [49] from pslibrary [50]. The pseudopotentials are reported in the note.\(^3\) The cutoff for the wave functions (charge density) was 60 Ry (400 Ry) for palladium, 45 Ry (300 Ry) for platinum, 60 Ry (1200 Ry) for copper and 60 Ry (400 Ry) for gold. The presence of the Fermi surface has been dealt with by a smearing approach [33] with a smearing parameter \( \sigma = 0.005 \, \text{Ry} \) for palladium and platinum and \( \sigma = 0.02 \, \text{Ry} \) for copper and gold. The \( k \)-point mesh was 40 \( \times \) 40 \( \times \) 40 (except for PBEsol gold, for which a mesh 48 \( \times \) 48 \( \times \) 48 has been used). DFPT [30, 51] was used to calculate the dynamical matrices on a \( 8 \times 8 \times 8 \) \( q \)-point mesh for palladium and platinum (corresponding to 29 special \( q \)-points for configurations strained with \( \varepsilon_A \), 59 \( q \)-points for \( \varepsilon_E \) and 65 for \( \varepsilon_F \)) and \( 4 \times 4 \times 4 \) \( q \)-point mesh for copper and gold (corresponding to 8 \( q \)-points for configurations

\(^3\)For palladium we used Pd.pz-n-kjpaw_psl.1.0.0.UPF and Pd.pbesol-n-kjpaw_psl.1.0.0.UPF. For platinum Pt.pz-n-kjpaw_psl.1.0.0.UPF and Pt.pbesol-n-kjpaw_psl.1.0.0.UPF. For copper Cu.pz-dn-kjpaw_psl.1.0.0.UPF, Cu.pbe-dn-kjpaw_psl.1.0.0.UPF and Cu.pbesol-dn-kjpaw_psl.1.0.0.UPF. For gold we used Au.pz-dn-kjpaw_psl.0.3.0.UPF and Au.pbesol-dn-kjpaw_psl.0.3.0.UPF.
Table 1. ECs at $T = 0$ K computed with LDA, PBEsol and PBE exchange and correlation functionals compared with previous theoretical works and experimental data. The equilibrium lattice constants ($a_0$) are in Å while the ECs and the bulk moduli $B$ are in kbar. The bulk modulus is $B = \frac{1}{3}(C_{11} + 2C_{12})$.

| Material | $a_0$  | $C_{11}$ | $C_{12}$ | $C_{44}$ | $B$  |
|----------|--------|----------|----------|----------|------|
| Palladium |        |          |          |          |      |
| LDA      | 3.85   | 2696     | 2071     | 788      | 2279 |
| PBEsol   | 3.88   | 2445     | 1861     | 740      | 2056 |
| PBE      | 3.95   | 2010     | 1532     | 606      | 1690 |
| LDA$^a$  | 3.90   | 2743     | 1463     | 716      | 1890 |
| GGA$^b$  | 3.94   | 2548     | 1358     | 587      | 1755 |
| Expt.$^c$ | 3.896(2) | 2341(27) | 1761(27) | 712(3)  | 1954 |
| Platinum |        |          |          |          |      |
| LDA      | 3.90   | 3800     | 2759     | 802      | 3106 |
| PBEsol   | 3.92   | 3553     | 2581     | 764      | 2905 |
| PBE      | 3.98   | 3039     | 2234     | 615      | 2502 |
| LDA$^d$  | 3.91   | 3645     | 2665     | 736      | 2992 |
| PBEsol$^e$ | 3.91  | 3595     | 2456     | 858      | 2836 |
| GGA$^d$  | 3.99   | 3063     | 2133     | 730      | 2443 |
| Expt.$^f$ | 3.92268(4) | 3487(130)| 2458(130)| 734(20) | 2801(9) |
| Copper   |        |          |          |          |      |
| LDA      | 3.52   | 2349     | 1666     | 998      | 1894 |
| PBEsol   | 3.56   | 2100     | 1480     | 938      | 1687 |
| PBE      | 3.63   | 1775     | 1238     | 793      | 1417 |
| LDA$^g$  | 3.64   | 1678     | 1135     | 745      | 1316 |
| GGA$^h$  | 3.63   | 1745     | 1253     | 752      | 1417 |
| GGA$^i$  | 3.63   | 1800     | 1200     | 840      | 1400 |
| Expt.$^j$ | 3.596  | 1762.0   | 1249.4   | 817.7    | 1420.3 |
| Gold     |        |          |          |          |      |
| LDA      | 4.05   | 2120     | 1873     | 373      | 1955 |
| PBEsol   | 4.10   | 1926     | 1651     | 366      | 2614 |
| PBE      | 4.16   | 1544     | 1327     | 268      | 1389 |
| GGA$^k$  | 4.07   | 2021     | 1742     | 379      | 1835 |
| PBE$^l$  | 4.19   | 1478     | 1435     | 387      | 1449 |
| Expt.$^l$ | 4.062  | 2016.3   | 1696.7   | 454.4    | 1803.2 |

$^a$Reference [27].
$^b$Reference [35].
$^c$Reference [22] (room temperature $a_0$, $T = 0$ K extrapolation of ECs).
$^d$Reference [36].
$^e$Reference [15] (all electrons).
$^f$Reference [37] (room temperature results, most recent work).
$^g$Reference [13].
$^h$Reference [38].
$^i$Reference [39].
$^j$Reference [40] for $a_0$ and Reference [41] for the ECs ($T = 0$ K extrapolation).
$^k$Reference [42].
$^l$Reference [40] for $a_0$ and Reference [43] for the ECs ($T = 0$ K extrapolation).

strained with $\epsilon_A$ and 13 $q$-points for those strained with $\epsilon_E$. For palladium and platinum a thicker $q$-points mesh was necessary due to the presence of Kohn anomalies [8]. For all materials the dynamical matrices have been Fourier interpolated on a $200 \times 200 \times 200$ $q$-point mesh to evaluate the vibrational free-energy. The calculation of the TDECs is done by `thermo_pw` as described in reference [20]. The grid of reference geometries was centered at the minimum of the total energy as reported in table 1 except for the LDA study of platinum that was centered at $a_0 = 3.916$ Å. We used 7 reference geometries separated by $\Delta a = 0.07$ a.u. for all metals except for platinum where we used $\Delta a = 0.0233$ a.u. for LDA and $\Delta a = 0.03$ a.u. for PBEsol due to the presence of unstable strained configurations with imaginary phonon frequencies at
too large lattice constants. We used 6 strained configurations for each type of strain with a strain interval $\delta c = 0.005$. In total we computed the phonon dispersions on 126 geometries for each material and functional in addition to those computed on the reference configurations required to compute $\alpha(T)$ and the thermal expansion. For the electronic calculation we computed the bands in all the reference configurations (to include the effect on $\alpha(T)$) and in all the strained ones (to include it in the TDECs). The k-point mesh for the electronic DOS calculations was $48 \times 48 \times 48$. We use a Gaussian smearing with a smearing parameter of 0.01 Ry. The inclusion of the electronic finite temperature effect in the thermodynamic quantities and in the TDECs is documented in the theoretical PW user’s guide.

In order to fit the free-energy as a function of the strain we used a polynomial of degree two because, although the use of a fourth-degree polynomial could introduce some differences, it requires higher cutoffs to converge the $T = 0$ K ECs. To interpolate the ECs computed at the different reference configurations and calculate them at the temperature dependent geometry we use a fourth-degree polynomial. More informations about the convergence tests are reported in the supplementary material (https://stacks.iop.org/JPCM/33/475901/mmedia).

The DFPT finite-temperature approach was applied to evaluate the ECs of platinum at the temperatures $T_{FD} = 800$ K (with a Fermi–Dirac smearing $\sigma_{FD} \approx 0.005$ Ry) and $T_{FD} = 1000$ K ($\sigma_{FD} \approx 0.0063$ Ry). For this purpose the TDECs calculation was set in a single reference geometry with the lattice constant at the considered temperature: 7.429 a.u. for 800 K and 7.446 a.u. for 1000 K.

4. Applications

In table 1, we report the zero temperature lattice constants, ECs, and bulk moduli of the four metals calculated with different exchange and correlation functionals. We compare them with experiments and previous theoretical works. As usually found, PBE and PBEsol give slightly larger lattice parameters than LDA and smaller $T = 0$ K ECs. PBEsol reproduces the experimental ECs of palladium and platinum better than LDA and PBE with errors smaller than about 1% for all the ECs, compared to LDA errors in the range 10–18% in palladium and from $\approx 9\%$ ($C_{11}$ and $C_{44}$) to $\approx 12\%$ ($C_{12}$) in platinum. PBE has differences till to $\approx 15\%–16\%$ for both materials.

On the other hand, the experimental ECs of copper are well reproduced by PBE with errors equal or smaller than 3%, compared with errors larger than 15% for the other functionals. The LDA and PBEsol have almost the same accuracy in reproducing the $T = 0$ K $C_{11}$ and $C_{44}$ of gold (with errors of $\approx 5\%$ and $\approx 18\%$, respectively), while for the $C_{12}$ PBEsol has an error of $\approx 3\%$ and LDA an error of $\approx 10\%$, PBE has errors of $\approx 22\%$ in $C_{11}$ and $C_{12}$ and $\approx 40\%$ in $C_{44}$.

The differences found for the LDA ECs of palladium with respect to those of reference [27] are $\approx 2\%$ for $C_{11}$, $\approx 29\%$ for $C_{12}$ and $\approx 10\%$ for $C_{44}$. For platinum, comparing our LDA ECs with the calculations of reference [36] we found differences of $\approx 4\%$ for $C_{11}$, $\approx 3\%$ for $C_{12}$ and $\approx 8\%$ for $C_{44}$; while the comparison of our PBEsol ECs with the corresponding PBEsol all-electrons calculation of reference [15] gives differences of $\approx 1\%$ for $C_{11}$, $\approx 5\%$ for $C_{12}$ and $C_{44}$. The differences found for the LDA–ECs of copper with respect to those of reference [13] are $\approx 28\%$ for all ECs, while the differences between our PBE ECs with the other GGA ECs of references [38, 39] are smaller than $\approx 3\%$ for $C_{11}$ and $C_{12}$ and $\approx 5\%–6\%$ for $C_{44}$. Our PBEsol ECs of gold are close to the GGA estimates of reference [13] with differences of $\approx 5\%$ for $C_{11}$ and $C_{12}$ and $\approx 3\%$ for $C_{44}$. For reference, in palladium, platinum, and gold we report GGA ECs found in literature. As expected, they are smaller than our LDA and PBEsol ECs. They shows some differences with our PBE estimates, which are, however, very close to the PBE ECs reported in the materials project database and computed with the PAW method.

In figures 1–4 we report the TDECs of the four metals. For each plot we follow the same color-line convention: Red indicates LDA estimates, green PBEsol and blue, present only in copper, PBE. The continuous lines are computed by considering all contributions in the Helmholtz free-energy, while the dashed lines have been obtained neglecting the contribution of the electron thermal excitations. Black points are the experimental data.

The TDECs of palladium are shown in figure 1. Two experimental data-set are reported. The variation of the experimental ECs of reference [22] in the range 0–300 K is $3\%$ for $C_{11}$, about 0% for $C_{12}$ and $-1\%$ for $C_{44}$ with respect to the 0 K ECs. The corresponding LDA (PBEsol) variations in the same range of temperature are 3.7% (4.5%) for $C_{11}$, 2% (2%) for $C_{12}$ and $C_{44}$.
and 3.8% (3.8%) for $C_{44}$. In the range $T = 300–1200$ K the variations in the data of reference [24] are 7.3% for $C_{11}$, 6.4% for $C_{12}$ and 7.8% for $C_{44}$, while the corresponding theoretical softenings are 15% for $C_{11}$, 13% for $C_{12}$, 11% for $C_{44}$ for both functionals. Hence, both functionals give a similar temperature dependence. At room temperature the details of the experimental anomalies are not reproduced and above room temperature the theoretical softening is larger than the experimental one. The electronic effect is very small in $C_{11}$ and $C_{12}$ but leads to appreciable modifications of $C_{44}$ which becomes closer to the experiment. As expected, the electronic contribution increases with temperature and influences the softening of $C_{44}$ that without the electronic effect would be 20% in the range 300–1200 K.

The TDECs of platinum are reported in figure 2. From $T = 0$ K to $T = 1200$ K the experimental ECs decrease of about 24% for $C_{11}$, about 2% for $C_{12}$ and about 6% for $C_{44}$. The corresponding theoretical softening for LDA (PBEsol) are 18% (20%) for $C_{11}$, 11% (10%) for $C_{12}$ and 19% (19%) for $C_{44}$. Hence, the variation of $C_{11}$ is well reproduced while the other two ECs’ softenings are overestimated. As found for palladium, the electronic contribution is important and improves the comparison with the experiment only for the $C_{44}$ EC: without the electronic effect the softening would be $\approx 30\%$. However, it cannot describe the anomalies. In order to further investigate the trend of the ECs of platinum we also considered the effect of the electronic excitation on the phonon frequencies for the temperatures $T = 800$ K and $T = 1000$ K with the method explained in the previous section (results are reported in red circles in the plot, only for the LDA case). The red points are exactly over our curves (apart for a slight deviation in the $C_{11}$ at 1000 K). This fact points out that the electron–phonon interactions that modify the phonon frequencies have negligible consequences on the TDECs. We observe that our estimate of the electronic contribution is smaller than the one of reference [26] even for the $C_{44}$. In our calculation the largest contribution is the vibrational one which always decreases the ECs as the temperature increases. In reference [26] the vibrational contribution is described within a quasi-static framework which leads to an underestimation of the ECs’ softening. Our results are qualitatively closer to those of reference [27] that finds a conventional temperature dependence for the $C_{44}$.

The results of copper are shown in figure 3. Since the two different experimental set of data are smoothly connected we report the whole softening in the range of temperature $T = 0–800$ K: 15% for $C_{11}, 10\%$ for $C_{12}$ and 24% for $C_{44}$. The corresponding theoretical softening for LDA (PBEsol, PBE) are 13.5% (14%, 17%) for $C_{11}$, 7.6% (8.5%, 10.5%) for $C_{12}$ and 21% (21%, 26%) for $C_{44}$. The temperature dependence is almost the same for LDA and PBEsol, slightly larger for PBE. The estimated softenings agree very well with the experiment. PBE results are the closest to the experiment, reflecting the trend of the $T = 0$ K ECs shown in table 1. The electronic

Figure 2. Quasi-harmonic adiabatic ECs of platinum. LDA (red curves) is compared with PBEsol (green curves). The results obtained with the total free-energy (continuous line) are compared with those in which the contribution of electronic excitations is neglected (dashed lines). The red circles at 800 K and 1000 K are computed within the LDA by using the Fermi–Dirac occupations. Experimental data are taken from Collard and McLellan [25] (black triangles).

Figure 3. Quasi-harmonic adiabatic ECs of copper. LDA (red curves), PBEsol (green curves) and PBE (blue) are compared. The results obtained with the total free-energy (continuous line) overlaps those in which the contribution of electronic excitation is neglected (dashed lines). Experimental data are taken from Overton and Gaffney [41] (black triangles) and Chang and Himmel [52] (black circles).
In this paper we investigated the TDECs of palladium, platinum, copper, and gold by means of the QHA. LDA and GGA give almost the same softenings but differ in the zero temperature values. This work shows that PBEsol is the best choice for palladium, platinum, and gold. PBE is the best for copper. Moreover, we addressed the role of the thermal electronic excitations and found a negligible effect on the TDECs of copper and gold, and an improvement in the agreement with the experimental $C_{44}$ of palladium and platinum. Even though the computed softenings of all ECs is in reasonable agreement with the experimental ones, we could not reproduce the precise behavior of the anomalies in platinum and palladium. In platinum, we further investigated the effects of the change of the phonon frequencies induced by the finite temperature thermal electronic excitations, finding that it is small, even at the highest studied temperature $T = 1000$ K. At the current stage the discrepancy between theory and experiment in palladium and platinum is not solved and might require either a more sophisticated functional than LDA or GGA or a method that includes the anharmonic effects beyond the QHA approximation [53]. Since the experimental data are quite old, also a novel measurement of the TDECs could be useful.

Acknowledgments

Computational facilities have been provided by SISSA through its Linux Cluster and ITCS and by CINECA through the SISSA-CINECA 2019–2021 Agreement.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

References

[1] Saunders N and Miodownik A P 1998 CALPHAD (Oxford: Pergamon)
[2] Lukas H L, Fries S G and Sundman B 2007 Computational Thermodynamics (Cambridge: Cambridge University Press)
[3] Curtarolo S et al 2012 Comput. Mater. Sci. 58 218–26
[4] Touloukian Y S, Kirby R K, Taylor R E and Desai P D 1975 Thermal Expansion: Metallic Elements and Alloys (New York: Plenum)
[5] Hohenberg P and Kohn W 1964 Phys. Rev. 136 B864–71
[6] Kohn W and Sham L J 1965 Phys. Rev. 140 A1133–8
[7] Grabowski B, Hickel T and Neugebauer J 2007 Phys. Rev. B 76 024309
[8] Dal Corso A 2013 J. Phys.: Condens. Matter. 25 145401
[9] Dal Corso A 2014 https://dalcoroso.github.io/thermo_pw
[10] Palumbo M and Dal Corso A 2017 Phys. Status Solidi B 254 1700101
[11] Palumbo M and Dal Corso A 2017 J. Phys.: Condens. Matter. 29 395401
[12] Malica C and Dal Corso A 2019 Acta Crystallogr. A 75 624–32
[13] Wang H and Li M 2009 Phys. Rev. B 79 224102
[14] Goleosorkhtabar R, Pavone P, Spitaler J, Puschning P and Draxl C 2013 Comput. Phys. Commun. 184 1861–73
[15] Jamal M, Jalali Asadabadi S, Ahmad I and Rahnamaye Aliabad H A 2014 Comput. Mater. Sci. 95 592–9
[16] Karki B B, Wentzcovitch R M, de Gironcoli S and Baroni S 1999 Science 286 1705–7
[17] Dragoni D, Ceresoli D and Marzari N 2015 Phys. Rev. B 91 104105
[18] Steneteg P, Hellman O, Vekilova O Y, Shulumba N, Tasnádi F and Abrikosov I A 2013 Phys. Rev. B 87 094114
[19] Dal Corso A 2016 J. Phys.: Condens. Matter. 28 075401
[20] Malica C and Corso A D 2020 J. Phys.: Condens. Matter. 32 315902
[21] Malica C and Dal Corso A 2020 J. Appl. Phys. 127 245103
[22] Rayne J A 1960 Phys. Rev. 118 1545
[23] Weinmann C and Steinemann S 1974 Solid State Commun. 15 281
[24] Yoshihara M, McLellan R B and Brotzen F R 1987 Acta Metall. 35 775–80
[25] Collard S M and McLellan R B 1992 Acta Metall. Mater. 40 699
[26] Keuter P, Music D, Schnabel V, Stuer M and Schneider J M 2019 J. Phys.: Condens. Matter. 31 225402
[27] Liu Z-L, Yang J-H, Cai L-C, Jing F-Q and Alfè D 2011 Phys. Rev. B 83 144113
[28] Nye J F 1985 Physical Properties of Crystals (New York: Oxford Science Publications)
[29] Barron T H K and Klein M L 1965 Proc. Phys. Soc. 85 523
[30] Baroni S, de Girolami S, Dal Corso A and Giannozzi P 2001 Rev. Mod. Phys. 73 515
[31] Zhang X, Grabowski B, Körmann F, Freysoldt C and Neugebauer J 2017 Phys. Rev. B 95 165126
[32] Mermin N D 1965 Phys. Rev. 137 A1441–3
[33] Methfessel M and Paxton A T 1989 Phys. Rev. B 40 3616–21
[34] de Girolami S 1995 Lattice dynamics of metals from density-functional perturbation theory Phys. Rev. B 51 6773–6
[35] Gao T and Kitchin J R 2018 Catal. Today 312 132–40
[36] Razumovskiy V I, Isaev E I, Ruban A V and Korzhavyi P A 2008 Intermetallics 16 982–6
[37] Kamada S et al 2019 C. R. Geosci. 351 236
[38] Yue-Lin L, Li-Jiang G and Jin S 2012 Chinese Phys. B 21 096102
[39] Jahnátek M, Hafner J and Krajčí M 2009 Phys. Rev. B 79 224103
[40] Haas P, Tran F and Blaha P 2009 Phys. Rev. B 79 085104
[41] Overton W C and Gaffney. J 1955 Phys. Rev. 98 969
[42] Kong G-X, Ma X-J, Liu Q-J, Li Y and Liu Z-T 2018 Physica B: Condensed Matter 533 58–62
[43] Neighbours J R and Alers G A 1958 Phys. Rev. 111 707–12
[44] Giannozzi P et al 2009 J. Phys.: Condens. Matter. 21 395502
[45] Giannozzi P et al 2017 J. Phys.: Condens. Matter. 29 465901
[46] Perdew J P and Zunger A 1981 Phys. Rev. B 23 5048–79
[47] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865–8
[48] Perdew J P, Ruzsinszky A, Csonka G I, Vydrov O A, Scuseria G E, Constantin L A, Zhou X and Burke K 2008 Phys. Rev. Lett. 100 136406
[49] Blöchl P E 1994 Phys. Rev. B 50 17953
[50] Dal Corso A 2010 https://github.com/dalcorso/pslibrary
[51] Dal Corso A 2010 Phys. Rev. B 81 075123
[52] Chang Y A and Himmel L 1966 J. Appl. Phys. 37 3567–72
[53] Shulumba N, Hellman O, Rogström L, Raza Z, Tasnádi F, Abrikosov I A and Odén M 2015 Appl. Phys. Lett. 107 231901