High-pressure Debye-Waller and Grüneisen parameters of Au and Cu

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Abstract. The lattice vibrations are determined in the quasi-harmonic approximation for elemental Au and Cu to twice their normal density by first-principles electronic band-structure calculations. It is found for these materials that the important moments of the phonon density of states can be obtained to high accuracy from short-ranged force constant models. We discuss the implications for the Grüneisen parameters on the basis of calculated phonon moments and their approximations by using bulk moduli and Debye-Waller factors.

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Accurate and reliable high-pressure standards are fundamental for the study of matter under extreme conditions and in the earth sciences. With the advent of neutron and x-ray diffraction measurements up to several hundred GPa in diamond anvil cells it becomes important to be able to determine precisely the pressure. At high pressures the equation of state (EOS) of elemental metals are commonly used as pressure scales. However, these scales are based on either extrapolation of low-pressure data or reduction from the Hugoniot to room temperature. The reduction of the Hugoniot curve onto $P-V$ isotherms requires model assumptions about the Grüneisen parameter, which are experimentally not well founded. Our ability to calculate accurate moments of the phonon distribution from first-principles electronic structures enables us to strongly constrain the Grüneisen parameter and to establish an accurate EOS and high-pressure standard for elemental gold and copper. This is an important step toward high-precision high-pressure experiments.

Since recent experiments raised concerns about the consistency of these standards [1], we revisited the problem of high-pressure standards using a semi-empirical approach combined with first-principles electronic structure calculations [2]. This method is different from the tight-binding approach that was earlier applied to solid copper [3]. We determined the lattice vibrational contribution to the EOS in the quasi-harmonic approximation of elemental face centered cubic Au and Cu by first-principles electronic structure calculations. We found that the important moments of the phonon density of states can be obtained to high accuracy from short-ranged force constant models.

In this paper, we present the implications for the Grüneisen parameter based on those calculations and their approximations by using bulk moduli and Debye-Waller factors which, in principle, can be obtained from ultrasound and neutron/x-ray diffraction measurements. The accuracy of our results is based on the accuracy of first-principles electronic structure calculations, which were performed in the local-density approximation (LDA) and generalized-gradient approximation (GGA) of density functional theory. From these results elastic moduli and zone boundary phonon frequencies were obtained. Fitting simultaneously a short-ranged, second nearest-neighbor Born-von Kármán (BvK) force matrix model to the zone boundary frequencies and the elastic moduli enabled us to generate phonon dispersion curves in the entire Brillouin zone and to compute any phonon moment needed, which is typically accurate within a few percent.

At high temperatures, i.e., in the classical limit, the temperature dependence of the pressure of a solid is dominated by the contribution from lattice vibrations, $P_{vib}$. Its temperature derivative at constant volume, $(\partial P_{vib}/\partial T)_V$, is proportional to the Grüneisen parameter $\gamma$, which is defined by

$$\gamma = -\sum_k \frac{d \ln \omega_k}{d \ln V} = -\frac{d \ln \omega_0}{d \ln V},$$

where the phonon frequencies $\omega_k$ are functions of volume only and the summation is over all eigenmodes. Eq. (1) defines the logarithmic phonon moment $\omega_0$.

For practical reasons one often uses an interpolating Debye phonon model for calculating the EOS or for ana-
lyzing diffraction data, instead of the more elaborate lattice dynamical models. Since in a Debye phonon model the Debye frequency \( \omega_D \) is identical to all other phonon moments, the approximation \( \omega_D \approx \omega_n \), with \( n \geq -3 \), is widely used for computing lattice vibrational properties and Grüneisen parameters. The moments \( \omega_{-2} \) and \( \omega_{-3} \) are related to the Debye-Waller factor at high temperatures and the sound velocity, respectively \[7\]. Using the theoretical relationships for the thermal mean-square displacement of an atom, \( \langle u^2 \rangle \propto T/\omega^2 \), and the sound speed, \( c \approx \omega_{-3} \approx \sqrt{B/V^{3/2}} \), we find the following approximations to the Mie-Grüneisen theory for the high-temperature Grüneisen parameter,

\[
\gamma \approx \gamma_h = \left(\frac{1}{6} - \frac{1}{2} \frac{d \ln B}{d \ln V}\right) \quad (2)
\]

\[
\gamma \approx \gamma_{DW} = \left(\frac{1}{2} \frac{d \ln \langle u^2 \rangle}{d \ln V}\right) \quad (3)
\]

The derivation of Eq. (2) requires a constant Poisson ratio (Slater approximation). Moruzzi et al. \[9\] studied extensively its application to the 4d transition elements and found good agreement with experiment at ambient conditions. The advantage of using Eq. (2) for estimating the Grüneisen parameter is that it is readily accessible from ultrasound and diffraction measurements. On the other hand, the expression for the thermal parameter in Eq. (3) has not seen much application, because of the extreme difficulties of measuring accurate thermal mean-square displacements in high-pressure diffraction experiments \[10\]. Since these different approximations of the Grüneisen parameter emphasize different phonon frequencies in the Brillouin zone compared to the log-moment \( \omega_0 \), we do expect to find deviations from \( \gamma \) by at least several percent, when using these approximate formulas, reflecting the differences between different phonon moments.

The calculation of the phonon moments \( \omega_0 \) requires knowledge of the phonon frequencies for all \( k \) points in the Brillouin zone \[7\]. The direct first-principles calculation of frequencies on a dense \( k \) mesh is computationally intensive, while the phonon dispersions of most elements can be easily parameterized using lattice dynamical models like a generalized BvK force matrix model. Often it suffices to use a short-ranged force model to compute the low order moments accurately within a few percent \[11\]. In particular, for elemental Au and Cu the log-moment \( \omega_0 \) is converged to less than 1% with a 2nd nearest-neighbor interatomic shell model at ambient conditions. Thus, we chose to calculate four zone boundary phonon frequencies corresponding to the transverse and longitudinal eigenmodes at the \( X \) and \( L \) points of the Brillouin zone. These are computed with standard frozen-phonon methods. Additionally, three elastic moduli are computed using the method by Söderlind et al. \[12\]. We fitted these results to a 2nd nearest-neighbor BvK force model, which then allows the evaluation of the frequencies \( \omega_0 \) in the entire Brillouin zone. Details of this calculation will be published elsewhere \[13\].

We fitted the theoretical \( \omega_0 \), \( B \), and \( \langle u^2 \rangle \) results to a functional form that gives a realistic \( V \)-dependence of the Grüneisen parameter, which has been used in many EOS calculations \[13\].

\[
\gamma(V) = \gamma^* + A_1 \left(\frac{V}{V_0}\right) + A_2 \left(\frac{V}{V_0}\right)^2 \quad (4)
\]

where \( V_0 \) is the volume at ambient pressure, \( \gamma^* \) is the infinite density limit of \( \gamma \), and \( A_1 \) and \( A_2 \) are fit parameters. Recently, it has been argued for the value \( \gamma^* = 1/2 \), instead of the commonly used \( \gamma^* = 2/3 \) \[14\]. However, our results are insensitive to this difference and hence we chose \( \gamma^* = 2/3 \). The corresponding fitted values are listed in Table 1.

In order to test the robustness of the calculated \( \gamma \) values using Eq. (4), we also fitted \( \omega_0 \), \( B \), and \( \langle u^2 \rangle \) to the widely used expression

\[
\gamma(V) = \gamma(V_0) \left(\frac{V}{V_0}\right)^q \quad (5)
\]

where the fit parameters \( \gamma(V_0) \) and \( q \) are listed in Table 2 see also the inserts of Figs. 1(b) and 2(b).

In Figs. (1) and (2) we show the normalized log-moments, bulk moduli, and thermal mean-square displacement parameters of elemental Au and Cu based on our first-principles calculations. To emphasize the very similar scaling behavior of these lattice dynamical properties, we normalized their values by their corresponding ambient condition values.

We used the functional forms for the Grüneisen parameter given in Eqs. (4) and (5) to integrate Eqs.

| \( B \) [GPa] | \( \omega_0/2\pi \) [THz] | \( \langle u^2 \rangle \) [pm\(^2\)] | \( \gamma \) | \( \gamma_h \) | \( \gamma_{DW} \) |
|---|---|---|---|---|---|
| Au | theo. | 167.7 | 3.49 | 83.2 | 2.99 | 2.76 | 3.03 |
| | exp. | 167 Ref. [4] | 3.65 Ref. [5] | 63 Ref. [6] | 2.95 Ref. [7] | |
| Cu | theo. | 149.5 | 6.86 | 61.7 | 1.85 | |
| | exp. | 137 Ref. [4] | 6.43 Ref. [5] | 76 Ref. [8] | 2.02 Ref. [7] | |
TABLE 2. Fit parameters and $\omega_0$, $B$, and $\langle \sigma^2 \rangle$ for Au and Cu at ambient conditions were obtained from fitting the theoretical data in Figs. 1(a) and 2(a) using Eq. 5. The reference values $\gamma_{\text{ref}}$ are from [7] and were derived using the thermodynamic definition of $\gamma = (V/C_V)(\partial P/\partial T)_V$, with the specific heat $C_V$.

|       | $\gamma_{\text{ref}}$ | $\gamma(V_0)$ | $\gamma(V_0)/B$ | $\gamma(V_0)/\omega_0$ | $q_B$ | $q_{DW}$ | $\omega_0/2\pi$ [THz] | $B$ [GPa] | $\langle \sigma^2 \rangle$ [pm$^2$] |
|-------|------------------------|----------------|------------------|------------------------|--------|----------|------------------------|----------|-------------------------|
| Au    | 2.95                   | 2.95           | 2.72             | 3.00                   | 1.229  | 1.064    | 1.481                  | 3.48     | 166.9                   | 83.8 |
| Cu    | 2.02                   | 1.85           | 2.29             | 1.68                   | 0.445  | 0.774    | 0.623                  | 6.86     | 149.1                   | 61.3 |

FIGURE 1. (a) Normalized (to ambient conditions) log-moment, bulk modulus, and thermal mean-square displacement of Au at $T = 296$ K from electronic structure calculations at $V/V_0 = 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1$. (b) Corresponding Grüneisen parameters using Eq. 4. $\gamma(V_0) = 2.95$ [7] (cross) is shown for reference. Insert: Corresponding Grüneisen parameters using Eq. 5.

FIGURE 2. (a) Normalized (to ambient conditions) log-moment, bulk modulus, and thermal mean-square displacement of Cu at $T = 296$ K from electronic structure calculations at $V/V_0 = 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1$. (b) Corresponding Grüneisen parameters using Eq. 4. $\gamma(V_0) = 2.02$ [7] (cross) is shown for reference. Insert: Corresponding Grüneisen parameters using Eq. 5.

This allowed us to fit the theoretical log-moments, bulk moduli, and thermal parameters and to extract the fitting parameters necessary for calculating the corresponding Grüneisen parameters shown in Figs. (1b) and (2b).

We found for the volume compressions considered here that $\gamma$ of Au and Cu are quite well described by either expression 4 or 5. The differences in the calculated $\gamma$ values are only a few percent. A detailed discussion of the accuracy of the different functional forms for $\gamma(V)$ and its consequences for the equation of state and the Hugoniot is given in Ref. [3]. In the case of Au, the approximate expressions for the Grüneisen parameter in Eqs. 2 and 3 give good agreement with the correct high-temperature $\gamma$ obtained from Eq. 1. The deviations of $\gamma_B$ and $\gamma_{DW}$ from $\gamma$ are mostly less than 8%. In the case of Cu, the deviations of $\gamma_B$ and $\gamma_{DW}$ from $\gamma$ are generally bigger than for Au, but never more than 15% for compressions in the range $0.5 < V/V_0 < 1.0$. A possible explanation of the larger deviations for Cu may be that the Debye temperature and equivalently the log-moment of Cu are almost twice as large as for Au. Since the typical temperature of lattice vibrations of Cu, $\hbar \omega_0/k_B \approx 330$ K, is slightly above room temperature (300 K), one may have to go beyond the classical approximation for accurately calculating the Grüneisen parameter at ambient conditions.

Comparing $\gamma_{DW}$ and $\gamma_B$ with $\gamma$, we find in the range of compressions $0.8 < V/V_0 < 1.0$ that the Debye-Waller approximation $\gamma_{DW}$ results generally in better agreement with $\gamma$ than the approximation using the bulk modulus $\gamma_B$. This situation is reversed below $V/V_0 \sim 0.8$. At such high compression $\gamma_B$ is in very good agreement with $\gamma$ of Au and in good agreement for Cu, while $\gamma_{DW}$ deviates the most. A simple explanation of this very different behavior of $\gamma_B$ and $\gamma_{DW}$ at high compression, i.e., below $V/V_0 \sim 0.8$, is due to the drastic stiffening of the phonon frequencies and the simultaneous increase of the bulk
modulus with decreasing $V$. At such high pressures and room temperature the excited phonons probe mostly the linear part of the phonon dispersion. The slope of the dispersion near the zone center is crudely proportional to the bulk modulus, while the Debye-Waller factor averages all frequencies weighted by the temperature dependent occupation factor of each mode. Therefore, we expect Eq. (3) to fail when the temperature becomes comparable to the high-temperature Debye-Waller phonon moment. Roughly speaking, for $T$ of the order of the log-moment, $k_B T \sim \hbar \omega_0$.

In summary, we have successfully computed with high accuracy phonon moments of elemental gold and copper from first-principles electronic structure calculations combined with a Born-von Kármán force model. From the logarithmic phonon moments we calculated the volume dependence of the Grüneisen parameter up to twice the normal density of Au and Cu at ambient conditions. Comparing the Grüneisen parameter with approximations based on the bulk modulus and the Debye-Waller factor, we found that for low compression, $0.8 < V/V_0 < 1.0$, the approximation using the thermal mean-square displacement is more accurate than the one using the bulk modulus, while at higher compression the bulk modulus gives generally better agreement with $\gamma$. Therefore, a combination of $\gamma_B$ and $\gamma_{DW}$, which can be obtained from ultrasound and diffraction measurements, can give an estimate of the volume dependence of the Grüneisen parameter $\gamma$ within approximately 10%. This provides a useful alternative for determining the Grüneisen parameter besides using the thermodynamic relation, which depends on the knowledge of the bulk modulus, thermal expansion, and specific heat.

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