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THE ROLE OF THERMAL EXCITATION OF D BAND ELECTRONS IN ULTRAFAST LASER INTERACTION WITH NOBLE (Cu) AND TRANSITION (Pt) METALS

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ABSTRACT

The temperature dependences of the electron heat capacity and electron-phonon coupling factor for noble (Cu) and transition (Pt) metals are investigated based on the electron density of states (DOS) obtained from *ab initio* electronic structure calculations. For Cu, d band electrons could be thermally excited when the electron temperature exceeds ~3000 K, leading to a significant increase, up to an order of magnitude, in the electron-phonon coupling factor and strong enhancement of the electron heat capacity away from the linear dependence on the electron temperature, which is commonly used in most of the current computational and theoretical investigations of ultrafast laser interactions with metals. Opposite to the case in Cu, the thermal excitation of d band electrons in Pt leads to a monotonic decrease of the electron-phonon coupling factor and contributes to significant negative deviations of the electron heat capacity from the linear dependence in the range of electron temperatures that are typically realized in ultrafast laser material processing applications. Strong and drastically different temperature dependences of the thermophysical properties predicted for Cu and Pt point to the importance of the electron DOS effects and the necessity of full consideration of thermal excitation of d band electrons for realistic modeling of short pulse laser interaction with noble and transition metals.

1. INTRODUCTION

Ultrafast laser irradiation of a metal target can drive the target material into a highly nonequilibrium state where the electron temperature could be transiently brought up to very high values, comparable to the Fermi temperature, while the lattice remains relatively cold. For metals, the time evolution of the lattice and electron temperatures, T_l and T_e, is typically described with the two-temperature-model (TTM) [1]. The TTM model consists of two coupled non-linear differential equations that account for the laser excitation of the conduction band electrons and subsequent energy relaxation processes, i.e. energy transfer from hot electrons to the lattice vibrations due to the electron–phonon coupling and the electronic heat diffusion from the irradiated surface to the bulk of the target:

$$C_e(T_e)\frac{\partial T_e}{\partial t} = \nabla\left[K_e(T_e,T_l)\nabla T_e\right] - G(T_e)(T_e - T_l) + S(\vec{r},t) \quad (1)$$

$$C_l(T_l)\frac{\partial T_l}{\partial t} = G(T_e)(T_e - T_l) \quad (2)$$

where C and K are the heat capacities and thermal conductivities of the electrons and the lattice as denoted by subscripts e and l, $G(T_e)$ is the electron-phonon coupling factor related to the rate of the energy exchange between the electrons and the lattice, and $S(\vec{r},t)$ is a source term describing the laser energy deposition.

The success of the application of TTM for the quantitative description of the temporal and spatial evolution of the temperature and energy in an irradiated target relies in a big part on the realistic choice of temperature dependent thermophysical parameters in the TTM, Eqs. (1) and (2). At

high electron temperatures the thermophysical properties can be sensitive to the details of the electronic structure of the target material. It has been shown, in particular, that the electron heat capacity in Au [2,3] and Pt [4] can be directly affected by the thermal excitation of d band electrons. A systematic analysis of the temperature dependence of the thermophysical properties of Au, reported in Ref. [5], suggests that at high electron temperatures (>3000 K) the thermal excitation of d band electrons results in a significant increase of both the electron-phonon coupling factor and the electron heat capacity. These changes have strong implications on the predictions of TTM calculations. Therefore, the approximations commonly used in most of the current TTM calculations, namely, a linear temperature dependence of the electron heat capacity obtained from the Sömmerfeld expansion, which is valid only at very low electron temperatures [6], and a constant value for the electron-phonon coupling factor, are inappropriate for describing the material properties under conditions of strong ultrafast laser excitation.

In this paper we investigate the effects of thermal excitation of d band electrons on the temperature dependences of the electron heat capacity and electron-phonon coupling factor in Cu and Pt, two metals with very different electronic structures, typical for noble and transition metals. The electron DOS obtained from electronic structure calculations for Cu and Pt are discussed in Section 2. Results from the analysis of the temperature dependent thermophysical properties are presented in Section 3 and summarized in Section 4.

2. ELECTRONIC STRUCTURE CALCULATIONS

In order to investigate the effect of the electron DOS on the high temperature thermophysical properties of Cu and Pt, we perform electronic structure calculations based on the density functional theory using the *Vienna Ab-initio Simulation Package* (VASP) [7]. The Projector Augmented Wave (PAW) potential [8] is used in the calculation, where the exchange correlation term is treated within the Generalized Gradient Approximation (GGA). The calculations are done for Cu and Pt at the equilibrium lattice constants of 3.635 Å and 3.92 Å, respectively.

The electron DOS for Cu and Pt obtained from VASP at T_e=0 K are shown in Fig. 1. As a member of the noble metal family, Cu has a filled d band and an electronic structure similar to Au [5,6]. In the case of Pt, the Fermi level cuts through the partially filled d band, leading to a very high density of electron states at the Fermi level, typical for transition metals. By examining the electron DOS for Cu and Pt together with the Fermi distribution functions at various electron temperatures, one can see that for Cu at electron temperatures less than 0.1 eV (~10^3 K) only electrons around the Fermi level are excited, while at T_e ~ 1 eV (~10^4 K) or higher, the number of excited d band electrons can be significant and should be taken into account. For Pt, the d band electrons at energy levels around the Fermi energy can be easily excited even at low electron temperatures, shifting the Fermi level to higher energies and altering the thermophysical properties of the metal in a way different from what would be expected for the free electron model with a parabolic electron DOS [6].

3. TEMPERATURE DEPENDENCE OF THERMO-PHYSICAL PROPERTIES

In this section, the electron DOS obtained in Section 2 is used to investigate the temperature dependences of the electron heat capacity and electron-phonon coupling in Cu and Pt. The results are compared with approximations commonly used in most of the current TTM calculations.

3.1 Electron heat capacity $C_e(T_e)$

In general, the temperature dependence of the electron heat capacity in metals is described as [6]:

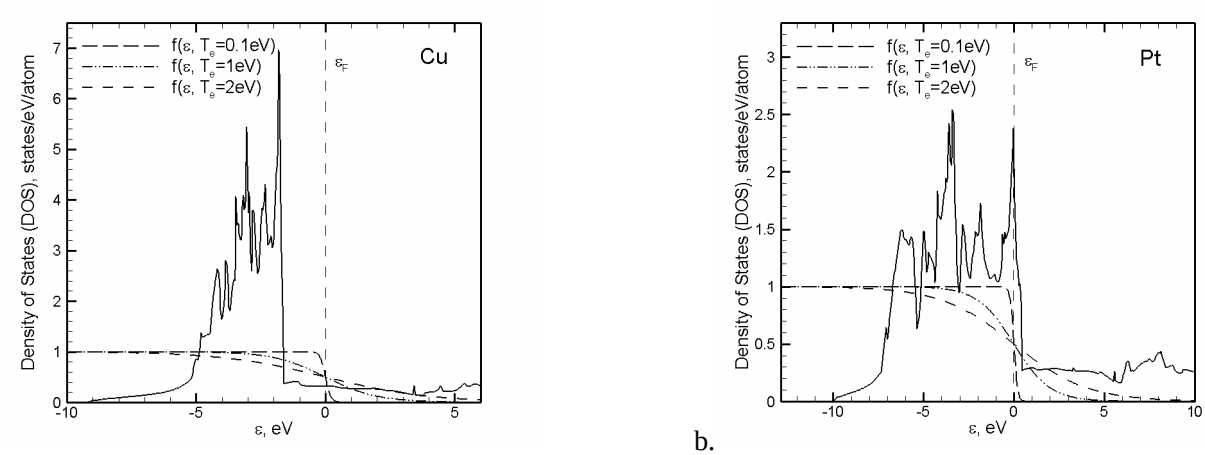

Figure 1. Electron DOS obtained in electronic structure calculations performed with VASP (solid lines) for (a) Cu and (b) Pt. The Fermi distribution functions are also shown for three different values of the electron temperature. The energy is shown with respect to the Fermi energy at zero temperature, ε_F.

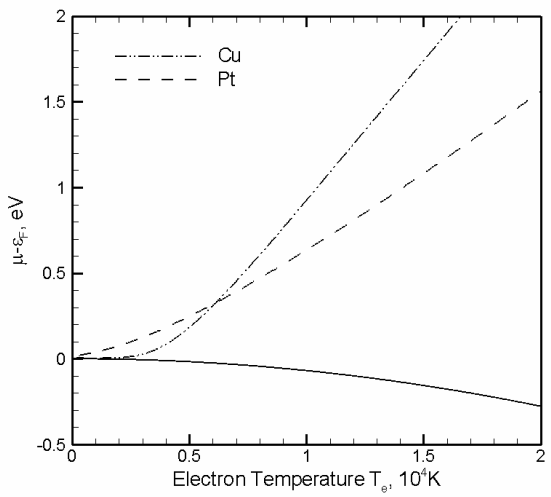

Figure 2. Chemical potential for Cu and Pt as a function of the electron temperature together with the chemical potential predicted by the free electron model (solid line). Results are shown with respect to the Fermi level at zero temperature, ε_F.

$$C_e(T_e) = \int_{-\infty}^{\infty} (\varepsilon - \varepsilon_F) \frac{\partial f(\varepsilon, \mu, T_e)}{\partial T_e} g(\varepsilon) d\varepsilon \qquad (3)$$

where $g(\varepsilon)$ is the electron DOS at the energy level ε, $f(\varepsilon, \mu, T_e)$ is the Fermi distribution function, defined as $f(\varepsilon, \mu, T_e) = \{\exp[(\varepsilon - \mu)/k_B T_e] + 1\}^{-1}$, ε_F is the Fermi energy at zero temperature, and μ is the chemical potential at T_e.

The evaluation of the electron heat capacity from Eq. (3) requires the knowledge of the chemical potential μ as a function of the electron temperature. The chemical potential can be found by setting the result of the integration of the product of DOS and the Fermi distribution function at T_e over all energy levels to be equal to the total number of electrons [6]. When the electron temperature is much lower than the Fermi temperature, for the free electron model the chemical potential can be approximated by the Sömmerfeld expansion for the electronic free energy:

$$\mu(T_e) = \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T_e}{\varepsilon_F} \right)^2 \right] \qquad (4)$$

Fig. 2 shows the chemical potentials for Cu and Pt calculated at various electron temperatures using DOS from VASP, together with the chemical potential predicted by the free electron model, i.e. Eq. (4). For Cu, when T_e is below ~3000 K, μ roughly follows the free-electron-like description, consistent with the good agreement of the shape of the DOS around the Fermi level with the prediction of the free electron model, Fig. 1(a). As the electron temperature exceeds ~3000 K, the thermal excitation from the high density of states at the edge of the d band leads to the increase of the chemical potential. In the case of Pt, the excitation from high density of states at energy levels below ε_F to small density of states above ε_F occurs at low electron temperatures, leading to the deviation of the chemical potential from the Sömmerfeld expansion even at low electron temperatures.

By incorporating the results for the chemical potential into Eq. (3), we obtain the electron heat capacity of Cu and Pt as a function of the electron temperature, Fig. 3. The results are shown together with the linear approximation $C_e(T_e) = \gamma T_e$ obtained from the Sömmerfeld expansion, which is valid only at low electron temperatures [6].

The difference in the temperature dependence of the electron heat capacity predicted for Cu and Pt can be understood from the following analysis. For Cu, below ~3000 K, the region of the electron DOS affected by thermal excitations ($k_B T_e$) is similar to the one predicted within the free electron model. As a result, the electron heat capacity follows the linear dependence, with the theoretical value of the coefficient γ calculated with the number density of s electrons in Cu, n_e = 1.0 atom^{-1}, as $\gamma = \pi^2 n_e k_B{}^2 / 2\varepsilon_F$ = 71 Jm^{-3}K^{-1} [6], being in a good agreement with the experimental value of 98 Jm^{-3}K^{-2} [9]. At electron temperatures exceeding 3000 K, the excitation from the large number of d states in Cu results in a positive deviation of the heat capacity from the linear temperature dependence. For Pt, the high density of electron states at the Fermi level ensures that the d electrons can be easily excited to the s band. The s band has a much smaller density of states and the shift of the chemical potential to higher energies, Fig. 2, leads to the negative deviation of the heat capacity from the linear dependence, Fig. 3(b).

Large deviations of the electron heat capacity from the linear dependence at high electron temperatures imply that the use of the linear approximation in TTM calculations can either significantly overestimate or underestimate the transient values of the electron temperature during the time of the electron-lattice nonequilibrium.

The electron thermal conductivity is related to the electron heat capacity through the Drude model relationship, $\kappa(T_e, T_l) = v_F^2 C_e(T_e) \tau_e(T_e, T_l) / 3$ where v_F is the Fermi velocity and $\tau_e(T_e, T_l)$ is the total electron scattering time with other electrons and the lattice [2,10]. Therefore, large positive or negative deviations of the electron heat capacity from the linear temperature dependence, shown in Fig. 3, would also affect the electron thermal conductivity, especially at the early stage of the electron-phonon equilibration, when the electron temperature is close to its maximum.

3.2 Electron-phonon coupling factor $G(T_e)$

The energy relaxation process between the excited hot electrons and the lattice in the irradiated target proceeds through the electron-phonon scattering processes, where the rate of the energy exchange is characterized by the electron-phonon coupling factor [11,12]. Despite the fact that a constant value for the electron-phonon coupling factor is

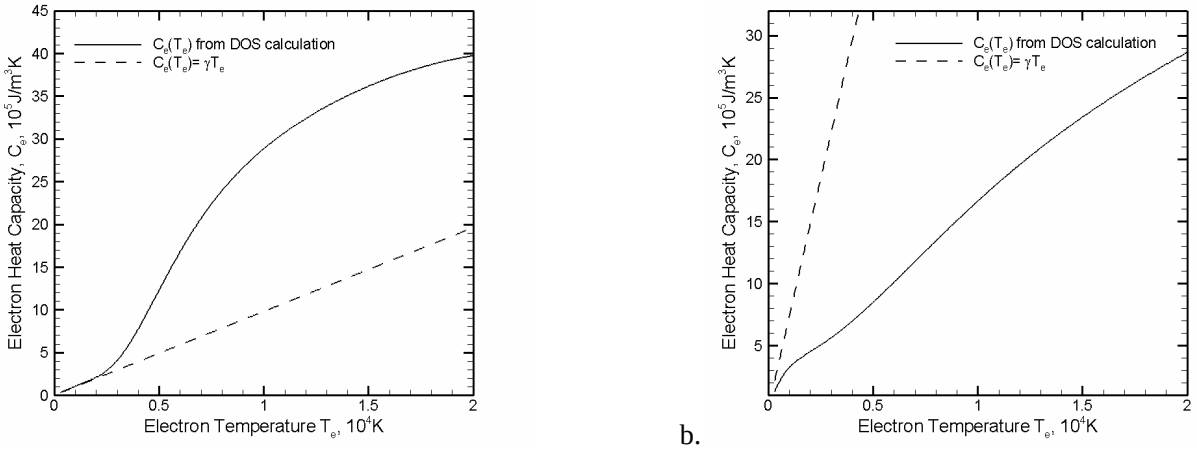

Figure 3. Electron heat capacity of (a) Cu and (b) Pt as a function of the electron temperature calculated with DOS obtained from VASP (solid lines) and using $C_e = \gamma T_e$ with (a) $\gamma = 98$ Jm^{-3}K^{-2} and (b) $\gamma = 740$ Jm^{-3}K^{-2} [9] (dashed lines).

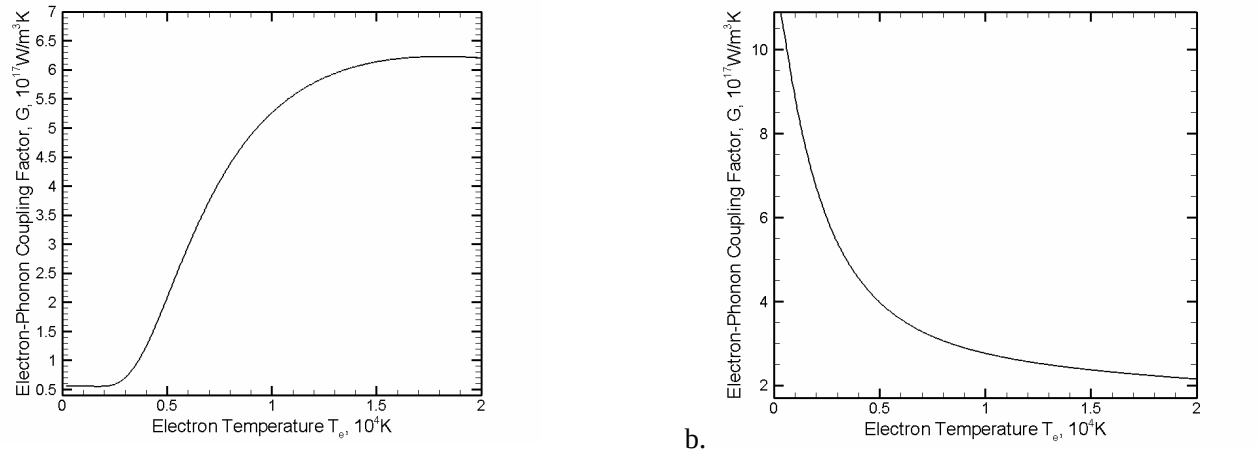

Figure 4. Electron-phonon coupling factor of (a) Cu and (b) Pt as a function of the electron temperature calculated with DOS obtained from VASP. Data presented in this figure is accessible in tabulated form from [15].

commonly used in most of the current computational and theoretical investigations of ultrafast laser interactions with metals, growing experimental evidence suggests that the application of the constant electron-phonon coupling may be inappropriate for strong laser excitation [2,13,14].

In order to explicitly account for the thermal excitation of d band electrons in noble and transition metals, we adopt the expression for the temperature dependent electron-phonon coupling factor obtained in Ref. [2]:

$$G(T_e) = \frac{\pi \hbar k_B \lambda \langle \omega^2 \rangle}{g(\varepsilon_F)} \int g^2(\varepsilon)(-\frac{\partial f}{\partial \varepsilon}) d\varepsilon \qquad (5)$$

where λ is the electron-phonon coupling constant defined in the superconductivity theory, $<\omega^2>$ is the second moment of the phonon spectrum defined by McMillan [16], and $g(\varepsilon_F)$ is the electron DOS at the Fermi level ε_F. At low electron temperatures, $-\partial f / \partial \varepsilon$ reduces to a delta function centered at the Fermi level ε_F and Eq. (5) recovers the expression for the electron-phonon coupling constant proposed by Allen in Ref. 11: $G_0 = \pi \hbar k_B \lambda \langle \omega^2 \rangle g(\varepsilon_F)$. At elevated electron temperatures, however, $-\partial f / \partial \varepsilon$ at energy levels away from ε_F becomes nonzero and the electron DOS $g(\varepsilon)$ at these energy levels needs to be taken into account in Eq. (5).

For Cu, with the value $\lambda<\omega^2>=29\pm4$ meV^2 measured in Ref. [17] and DOS shown in Fig. 1(a), we can determine the room temperature electron-phonon coupling constant from Allen's expression, $G_0 = (5.5\pm0.7)\times10^{16}$ Wm^{-3}K^{-1}. The literature values of G_0 for Cu vary between 1 and 20×10^{16} Wm^{-3}K^{-1} [18,19,20]. For Pt, due to absence of the experimental data for $\lambda<\omega^2>$, a value of $\lambda=0.66$ [21] from resistivity measurements and an approximation of $<\omega^2>=1/2\theta_D^2$ [22], where $\theta_D=240$ K is the Debye temperature for Pt [9], can be used to estimate the room temperature electron-phonon

coupling constant for Pt to be G_0~2.1×10^{18} $Wm^{-3}K^{-1}$. This value is of the same order of magnitude as the one evaluated from low temperature reflectivity measurements for Pt, $(1.09\pm0.5)\times10^{18}$ $Wm^{-3}K^{-1}$ [23]. As the verification of the value of $\lambda<\omega^2>$ for Pt is beyond the scope of this paper, and considering that the experimental value of the electron-phonon coupling constant in Ref. 23 is measured at relatively low electron temperatures, from room temperature up to ~465 K, we set the coupling factor at T_e=300 K in Eq. (5) to be equal to 1.09×10^{18} $Wm^{-3}K^{-1}$ and obtain $\lambda<\omega^2>$ = 142.5 meV^2. This value is then used in Eq. (5) to calculate the temperature dependence of the electron-phonon coupling factor in a broad range of electron temperatures as shown in Fig. 4(b).

The electron-phonon coupling factors of Cu and Pt calculated with Eq. (5) using the electron DOS obtained from VASP calculations are shown in Fig. 4 [15]. For Cu, the electron-phonon coupling factor remains close to a constant value below ~3000 K, similar to Au [5]. However, as the electron temperature exceeds ~3000 K, the increase of the coupling factor observed for Cu is significantly steeper as compared to Au. This observation can be related to the differences in the electron DOS of the two noble metals, Fig. 1(a) and Fig. 1 of Ref. [5]. The width of d band for Cu, ~3.5 eV, is much smaller than the one for Au, ~6 eV, resulting in a higher density of states at the high-energy edge of the d band in Cu as compared to Au. As a result, thermal excitation of d band electrons in Cu leads to a more significant increase in the electron-phonon coupling factor. In particular, the electron-phonon coupling factor for Cu exceeds the room temperature value by a factor of 9.5 at $T_e = 1\times10^4$ K, Fig. 4(a), compared to 5.8 for Au at the same electron temperature [5].

In the case of Pt, the strength of the electron-phonon coupling decreases monotonically as the electron temperature increases. This could be explained from the perspective of the role of thermal excitation of d band electrons in noble and transition metals. For Pt, as the thermal excitation of d band electron from below the Fermi level to higher energy levels leads to the increase in the chemical potential, Fig. 2, the contribution to the electron-phonon coupling from d band electrons is reduced, whereas for Cu the high value of DOS from d band ensures the significant contribution from d band electrons to the coupling, even though the chemical potential exhibits a temperature dependent behavior similar to Pt when the electron temperature is higher than ~3000 K. It should be noted that the trend of the decease in the strength of the electron-phonon coupling at high electron temperatures for Pt, Fig. 4(b), is consistent with the experimental value of 2.5×10^{17} $Wm^{-3}K^{-1}$, obtained from fitting the results of TTM calculations to the threshold laser fluences for the onset of surface melting in Pt films of different thickness [24]. From Fig. 4(b), the electron-phonon coupling factor for Pt decreases with respect to its room temperature value by a factor of 2.8 at $T_e = 0.5\times10^4$ K, by a factor of 3.9 at $T_e = 1\times10^4$ K, and by a factor of 5.1 at $T_e = 2\times10^4$ K.

The large changes in the strength of the electron-phonon coupling with increasing electron temperature, illustrated in Fig. 4, suggest that the commonly used assumption of the temperature-independent electron-phonon coupling can lead to either significant underestimation or overestimation of the electron-phonon energy exchange rate following a short pulse laser irradiation. An adequate description of the temperature dependence of the electron-phonon coupling factor is important for a reliable quantitative analysis of practically important characteristics of the laser-material interaction, such as threshold fluences for the onset of melting and ablation, strength of the laser-induced stress wave, and depth of the melting and/or heat-affected zone.

4. SUMMARY

The temperature dependences of the electron heat capacity and electron-phonon coupling factor are investigated for a noble metal Cu and a transition metal Pt based on the electronic structure calculations performed within the density functional theory. For Cu, there is no significant thermal excitation of d band electrons below ~3000 K, and the electron heat capacity follows a linear dependence on the electron temperature while the electron-phonon coupling remains constant. As the electron temperature exceeds ~3000 K, thermal excitation of electrons from the high-density edge of the d band leads to a steep and large (up to an order of magnitude) increase of the electron-phonon coupling factor and a significant positive deviation of the electron heat capacity from the linear dependence. For Pt, the shift of the chemical potential away from the large density of states around the Fermi level results in a monotonic decrease of the electron-phonon coupling factor with increasing electron temperature and negative deviations of the electron heat capacity from the linear dependence. The contrasting results obtained in this work for Cu and Pt suggest that the effect of thermal excitation of d band electrons on the thermophysical properties is sensitive to the structure of the electron DOS and a detailed analysis of the DOS effects is required for each target material.

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