Applied Surface Science 336 (2015) 79–84

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

First-principles calculations of heat capacities of ultrafast laser-excited electrons in metals

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ARTICLE INFO

Article history:
Received 1 July 2014
Received in revised form
22 September 2014
Accepted 22 September 2014
Available online 30 September 2014

Keywords:
Ultrashort laser
Femtosecond laser-excited electrons
First-principles calculations
Electronic heat capacities

ABSTRACT

Ultrafast laser excitation can induce fast increases of the electronic subsystem temperature. The subsequent electronic evolutions in terms of band structure and energy distribution can determine the change of several thermodynamic properties, including one essential for energy deposition; the electronic heat capacity. Using density functional calculations performed at finite electronic temperatures, the electronic heat capacities dependent on electronic temperatures are obtained for a series of metals, including free electron like, transition and noble metals. The effect of exchange and correlation functionals and the presence of semicore electrons on electronic heat capacities are first evaluated and found to be negligible in most cases. Then, we tested the validity of the free electron approaches, varying the number of free electrons per atom. This shows that only simple metals can be correctly fitted with these approaches. For transition metals, the presence of localized *d* electrons produces a strong deviation toward high energies of the electronic heat capacities, implying that more energy is needed to thermally excite them, compared to free *sp* electrons. This is attributed to collective excitation effects strengthened by a change of the electronic screening at high temperature.

1. Introduction

Material response to intense laser excitation is the subject of important research activities, and recent advances have revealed the determinant role of primary excitation events. Their accurate comprehension is necessary to correctly describe ultrafast structural dynamics [1,2], phase transitions [3,4], nanostruture formation [5], ablation dynamics [6,7], or strong shock propagation [8]. The interplay between ultrafast excitation and resulting excited material response still requires a comprehensive theoretical description for highly excited solid materials. Ultrashort laser irradiation produces a strong inhomogeneous heating of electrons that rapidly exchange energy through electron–electron collisions, leading the electronic subsystem to a thermalized state which is intimately related to the electronic structure of the material. This fast heating of the electronic subsystem leads in turn to a significant electron–phonon nonequilibrium, as the energy of the laser pulse is deposited before relaxation takes on and the material starts dissipating energy by thermal or mechanical ways.

During intense laser exposition, the irradiated material undergoes successive stages of extreme constraints, starting from the inhomogeneous excitation of electrons, the swift rise of electronic temperature and electronic pressure after thermalization of the electronic subsystem on the tens of femtosecond timescale [9]. These rapid processes are followed by the rise of the ionic temperature associated to thermally-triggered phase transitions, before ablating or returning to ambient conditions from further energy dissipations occurring at larger timescale. The accurate knowledge of these rapidly evolving conditions, in intensity and time, is of importance as they modify material properties. Evolution of electronic and ionic temperatures, T_e and T_i respectively, are generally calculated with the two-temperature model [10,11] which involved transient parameters such as electronic heat capacity, electron–phonon coupling strength, thermal conductivity, electronic pressure and material absorptivity.

The basic underlying assumption in the two-temperature model is that the electron subsystem consists of a thermalized population of a certain amount of electrons, a condition easily fulfilled in ablation processes conditioned by high electronic temperatures [7]. The energy evolution is determined by photon absorption, energy accumulation and thermal/mechanical transport (involving electron–electron and electron–phonon interaction) based on nonequilibrium dynamics. The effective number of charge carriers

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http://dx.doi.org/10.1016/j.apsusc.2014.09.146
0169-4332/

taking part in absorption, storage and dissipation of the energy has to be carefully evaluated to give a correct description of the evolution of the corresponding transient properties. A certain amount of free electrons responds collectively to the laser field through intraband transitions, associated to one-electron excitation corresponding to interband transitions. Modeling this absorption stage is rather complex, particularly for ultrashort laser irradiation as it initiates a strong charge disorder. The consequence of a nonthermal electron-ion population on the electronic energy storage is also of major importance. Finally, thermal and mechanical transports are often described by the concept of "free carriers", since mobility is required for these processes. Electronic pressure has been seen to follow a free electron like behavior at high T_e, even at solid density [12]. The electronic heat capacity C_e plays an important role since it connects the quantity of absorbed energy to the rise of the electronic temperature of the system, regardless to energy dissipation processes. Electronic heat capacities have been derived from post-treatment of first-principles calculations where electronic excitation was not fully taken into account [13,14]. Further, these quantities have been refined from density functional calculations dependent on the electronic temperature [12,15].

In this paper, the electronic heat capacity of a series of transition metals is discussed in detail, first according to various modeling conditions, considering the effect of the exchange and correlation energy functionals and then the effect of semicore electrons. C_e are then discussed in the framework of a free electron approach in order to evaluate the impact of d electrons of transition metals on this crucial thermodynamic quantity.

2. Calculation details

The modeling of Al, Ni, Cu, Au, Ti and W metals is performed with the code Abinit [16], which is based on plane-waves description of the wavefunctions. Calculations are carried out within the density functional theory [17,18] extended to finite electronic temperatures [19]. Projector augmented-waves atomic data [20] are used to take into account the effects of nuclei and core electrons. A cutoff energy of 40 Ha is applied to restrict the number of plane-waves and the Brillouin zone is meshed with a $30 \times 30 \times 30$ k-point grid using the Monkhorst–Pack method [21]. The local density approximation (LDA) [22] and the generalized gradient approximations (GGA) [23] are used with or without semicore electrons depending on the metals, in order to evaluate effects of semicore electronic states on computed properties. Computations are realized at the theoretical equilibrium lattice parameter of the crystal phase obtained at $T_i = 0$ K. Thus, electronic temperatures from 10^{-2} to 10^5 K are applied through a Fermi–Dirac distribution of electrons within a cold lattice. Such high T_e are conjectural and interrogate about phase stabilities. As we need to achieve a high temperature asymptotic behavior in this study, we will assume here that time and spatial conditions are not fulfilled for phase transitions to occur.

The calculated electronic heat capacity is derived from the variation of the internal energy E with respect to the electronic temperature as $C_e = \partial E/\partial T_e$. This thermodynamic quantity is computed for a series of metals at various T_e using LDA or GGA functionals with or without semicore electrons. Results are provided in Fig. 1 alongside the values of Lin et al. obtained from electronic structures calculated at $T_e = 0$ K [14]. At a first glance, the agreement between their results and ours is rather good for the low temperature range, the deviations appear at T_e above 4×10^4 K, where electronic structures start to react significantly to the heating of the electronic subsystem. In particular, transition and noble metals having a d-block within their valence band are sensitive to Fermi smearing,

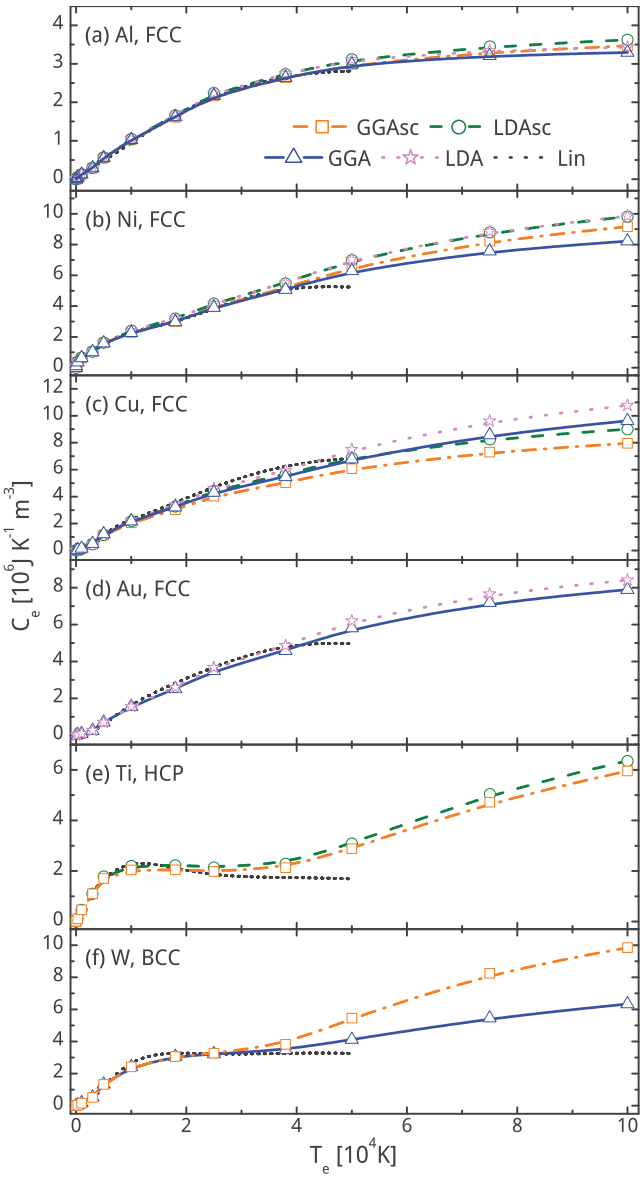

Fig. 1. Evolution of the electronic heat capacity with T_e for Al (a), Ni (b), Cu (c), Au (d), Ti (e), W (f), using different LDA and GGA exchange and correlation functionals. GGAsc and LDAsc indicate that the effect of semicore electrons are taken into account. The dotted black curves represent data of Lin et al. [14].

impacting d electron population, that induces a change of the electronic screening which in turn produces a significant energy shift of the d-block [4,12]. At high temperature, this produces a significant effect on the band structure, with consequences on the electronic heat capacities. The effect of exchange and correlation functional appears to be weak on computed C_e. The LDA method generally provides lower equilibrium parameters than the GGA, leading to slightly higher electronic electronic heat capacities per unit of volume.

The effect of semicore electronic states are also evaluated and Fig. 1(f) shows clearly that $4f$ semicore electrons of W have an impact at high T_e. Despite the fact that the 14 f electrons lie on deep states, around 19 eV below the valence band, they are significantly impacted by the increase of T_e starting from 4×10^4 K. For Al, Ni and Cu, the highest semicore electronic states correspond to $2p$ ones, they are located 50 eV below the valence band and are weakly impacted, even at high T_e. Nevertheless, a small effect of semicore electronic states is noticeable, with stronger C_e values for