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Road of warm dense noble metals to the plasma state: *Ab initio* theory of the ultrafast structural dynamics in warm dense matter

Fairoja Cheenicode Kabeer, Eeuwe S. Zijlstra, and Martin E. Garcia
Theoretische Physik, Universität Kassel and Center for Interdisciplinary Nanostructure Science and Technology (CINSaT), Heinrich-Plett-Straße 40, 34132 Kassel, Germany

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Intense ultrashort extreme ultraviolet (XUV) pulses can be used to create warm dense matter in the laboratory, which then develops to a plasma state. So far, however, it is unknown, whether this transition occurs via heat transfer from hot electrons to cold atoms or nonthermally due to a lattice instability. Here we computed the response of the phonon spectra of copper and silver to the presence of XUV-excited core holes and core holes together with very hot electrons. We found that the average interatomic bonds become stronger in the warm dense state. We discuss why these findings support the above-mentioned heat transfer scenario.

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Warm dense matter (WDM) is a new state of matter, which constitutes a challenge to modern physics and whose investigation offers excellent means to understand strongly correlated multiparticle systems and their fast dynamics. The strong excitation of electrons in solids by an extreme ultraviolet (XUV) pulse results in a two-temperature WDM state [1–4], a regime that is of great interest in high-pressure science [5], the geophysics of large planets [6], astrophysics [7], plasma production, inertial confinement fusion [8], and condensed-matter physics [9,10]. In the astrophysical context, WDM exists under stable and extreme density-temperature conditions, while in the laboratory, during the laser-matter interaction, WDM is generated as a transient (quasistationary for a short time) state between the condensed-matter and hot plasma regimes. While retaining the solid state density, it has two temperatures: The electronic temperature is of the order of tens of eV, and the ions remain cold and keep their original crystallographic positions [11]. In addition, an XUV pulse may excite core-level electrons [12–15]. So WDM is an intermediate state between condensed matter and the plasma, and the electrons effectively store the energy. Here we study the atomic pathways followed during the first few hundred femtoseconds in warm dense copper and silver and their role in the relaxation of WDM to equilibrium, i.e., into the plasma state [9,16–18]. This is an interesting problem, because it is in general not known whether this process occurs by nonthermal melting, where the atoms accelerate in the direction of a lattice instability [19], or thermally via the incoherent coupling of electrons and phonons, when the lattice has become sufficiently hot.

Insight into the dynamical properties of WDM can be obtained by studying the XUV-pulse-induced potential energy surface of the solid. As mentioned above, under strong XUV excitation, the electronic temperature T_e of solid dense Cu and Ag increases to the order of 10 000 K (corresponding to the laser energy deposited) while the lattice temperature T_l remains roughly unchanged. In addition, core holes may be generated. In this Rapid Communication we assumed that the interaction of an XUV pulse with Cu and Ag generates one core hole per primitive unit cell by the excitation of core-level electrons [17]. At room temperature and under ambient pressure, Cu (Ag) has a filled shell ionic core [Mg] $3p^6$ ([Zn] $4p^6$). We simulated the excitation of core holes by removing one core electron from a $3p_{3/2}$ orbital for Cu and one electron from a $4p_{3/2}$ orbital for Ag, respectively, and adding it to the conduction band in order to maintain charge neutrality. Core holes are very unstable and short lived and are expected to decay via Auger processes on a femtosecond time scale. However, they are excited again and again by the XUV pulse, making their influence non-negligible during the pulse duration. For an ultrashort XUV pulse we expect Cu and Ag atoms with one core hole to be close to their original lattice positions. So, at the instant an XUV pulse interacts with Cu or Ag, the system is in an exotic, highly ionized, yet crystalline state, of which the phonon spectrum is unknown. As the excited electrons and the other electrons in the system feel the potential produced by the core hole, we used the all-electron full-potential linearized augmented plane wave *ab initio* program WIEN2k [20], which explicitly includes the core electrons, in order to compute self-consistently screening effects and other changes in the total energy and atomic force constants (AFCs) of the system.

In order to obtain the AFCs one must assume that interactions between the atoms beyond a certain range are negligible. In our systems we neglected the forces beyond the sixth nearest neighbor distance, and the force constants were calculated by displacing an arbitrary (ith) atom from its equilibrium position ($\mathbf{R}_i$) along the $\alpha = z$ direction by $u_i^\alpha = 0.122$ and $0.139\ a_0$ (a_0 = Bohr radius) in Cu and Ag, respectively. Then the AFCs on the jth ($\mathbf{R}_j$) atom $A_{ij\alpha\beta}$ can be obtained by

$$A_{ij\alpha\beta} = -\frac{\partial F_j^\beta}{\partial u_i^\alpha}, \tag{1}$$

where F_j^β is the force on the jth atom produced due to the displacement u_i^α of the ith atom. The dynamical matrix of face-centered cubic (fcc) Cu and Ag over the first Brillouin zone (BZ), $D_{\alpha\beta}(\mathbf{q})$ was computed from the AFCs within a supercell of fixed volume containing 32 atoms using

$$D_{\alpha\beta}(\mathbf{q}) = \sum_j A_{ij\alpha\beta}\ \exp[-i\mathbf{q}\,(\mathbf{R}_i - \mathbf{R}_j)], \tag{2}$$

where $\mathbf{q}$ is the phonon wave vector. Diagonalization of $D_{\alpha\beta}(\mathbf{q})/M$, where M is the atomic mass, gave us phonon frequencies $\omega_i^2(\mathbf{q})$, $i = 1, \ldots, 3$.

TABLE I. Comparison of atomic force constants (AFCs) in mHa a_0^{-2} determined by interplanar force constant decomposition (Svensson *et al.*) [23], by decoupling transformation (Vanderwal) [22], and by DFT calculation (present work). The AFC label $n\alpha\beta$ refers to the displacement of the reference atom in the direction α and the resulting force on the nth nearest-neighbor atom in the direction β.

		Svensson *et al*	Vanderwal	DFT results		
Elements	AFC	(1967) results	(1977) results	Room temperature	Cold core hole	Hot core hole (30 000 K)
	1ZZ	−0.91	−0.74	−0.62	−2.80	−4.63
	1XY	9.52	9.57	8.71	17.15	19.56
	1XX	8.42	8.35	7.75	13.48	15.18
	2XX	0.23	0.29	0.72	3.72	3.59
	2YY	−0.15	−0.07	−0.27	−0.74	−0.34
Cu	3XX	0.41	0.36	0.41	0.22	0.07
	3YY	0.20	0.15	0.09	0.56	0.03
	3YZ	0.12	0.17	0.15	0.05	−0.02
	4XX	0.08	0.02	0.01	−0.55	0.04
	4ZZ	−0.19	−0.15	−0.02	−0.01	−0.01
	6XX	0.09	−0.04	−0.01	0.31	−0.01
	1ZZ			−0.99	−3.16	−3.98
	1XY			6.95	14.55	16.37
	1XX			6.15	11.48	12.65
	2XX			0.63	2.85	2.19
	2YY			−0.24	−0.58	−0.28
Ag	3XX			0.38	0.12	0.18
	3YY			0.09	0.35	0.08
	3YZ			0.13	−0.03	0.00
	4XX			0.12	−0.38	0.04
	4ZZ			−0.02	−0.02	−0.01
	6XX			−0.02	0.18	−0.01

To study the effect of T_e on the potential energy surface of WDM, the evolution of the phonon spectrum as a function of T_e was analyzed. We note that the electronic occupation numbers immediately following XUV excitation may be different from the Fermi distribution assumed in our present work. Even though electron-electron interactions quickly thermalize the electrons, the initial nonthermal occupancies may have a transient effect on the lattice properties that would be interesting to investigate but is outside the scope of the present communication. We performed our calculations with muffin-tin radii of 2.11 a_0 and 2.58 a_0 on the basis of the criterium that no more than 0.01 core electrons should "leak out" of their muffin-tin spheres, and $RK_{\max} = 8$ and 7 to fix the size of the basis sets for Cu and Ag, using a sufficiently fine **k** grid. We calculated the effects of various laser fluences by changing T_e within the framework of electronic-temperature-dependent density functional theory [21]. In addition, we analyzed the nonequilibrium state existing in the presence of one core hole per atom as well as hot electrons for the noble metals Cu and Ag.

Our computed AFCs for Cu and Ag with and without a core hole at two different T_e are presented in Table I. There are in total 11 inequivalent AFC acting in our supercells [22], whose directions we show in Fig. 1. A comparison of our computed AFC at room temperature with previous work [22,23] (Table I) indicates that they are in very good agreement. We further observed that the forces on the first nearest neighbors are affected most by the presence of a core hole.

In order to analyze the electronic-temperature-dependent potential energy surface, we determined the electronic and phonon densities of states (DOS) as well as the phonon dispersion spectra of our systems with one core hole per atom at various T_e up to 30 000 K. In Fig. 2 we see that the presence of core holes affects the materials in the same way as the presence of hot electrons alone [17], i.e., the AFCs of both Cu

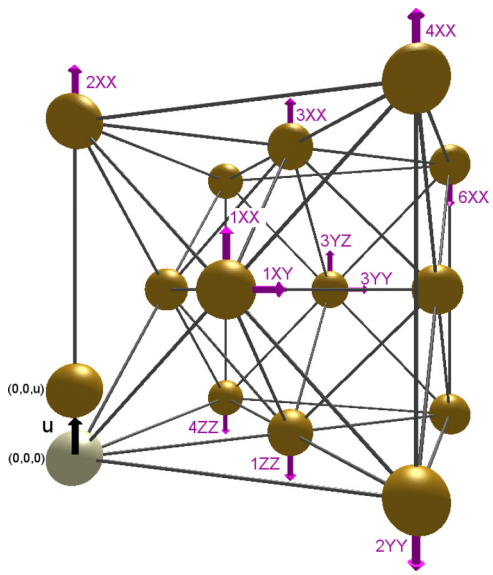

FIG. 1. (Color online) Face-centered cubic structure of a Cu crystal. The purple arrows indicate the directions of atomic forces up to sixth nearest neighbors when the reference atom at (0,0,0) is moved along the z direction to (0,0,u) by a small displacement u. The labels indicate atomic force constants and are the same as in Table I (room temperature).

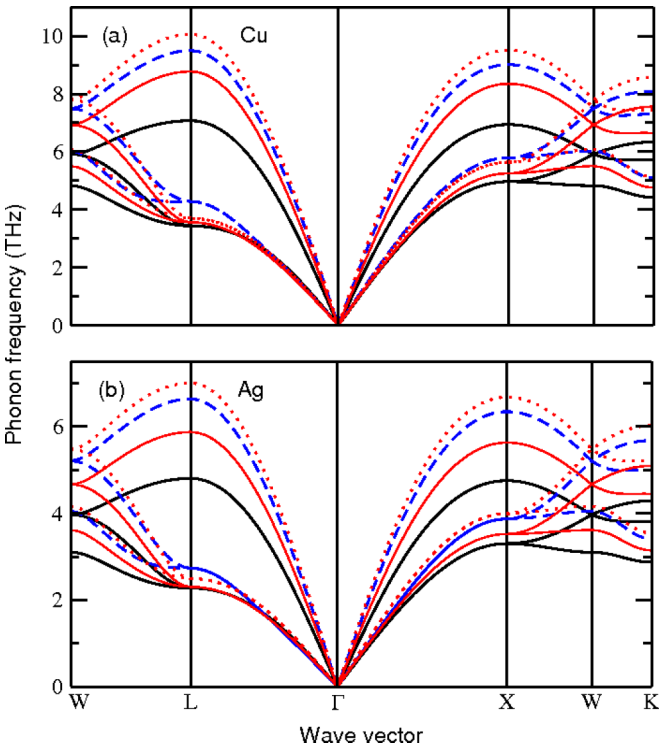

FIG. 2. (Color online) Phonon dispersion spectrum of (a) Cu and (b) Ag. Black solid curves show our results for room temperature, red solid curves at $T_e = 30\,000$ K without core hole. Blue dashed curves represent the state with one core hole per atom and red dotted curves are for the core-hole state with hot electrons at $T_e = 30\,000$ K.

and Ag increase and all phonon modes harden. In the presence of a core hole, however, the T_e affects the bonds differently: Most of the phonon modes are hardening, and few of them are softening. In both Cu and Ag, all longitudinal modes are showing hardening in the core-hole-excited state when T_e is raised from room temperature to 30 000 K (Fig. 2), but the transverse modes near the L and X points in the BZ of Cu and near the L point in the BZ of Ag are showing bond softening compared to the spectrum with a core hole. In more detail, Fig. 3 shows the temperature-dependent transverse and longitudinal acoustic phonon frequencies of Cu at the L point in the first BZ with one core hole per atom. The transverse acoustic [Fig. 3(a)] mode shows an increasing degree of softening with increasing T_e while the longitudinal acoustic [Fig. 3(b)] mode shows hardening upto 3000 K, then undergoes a weak softening until 12 000 K and a sharp hardening afterwards. Averaged over all modes in the first BZ the potential energy surfaces of both Cu and Ag harden in the warm dense regime as a function of T_e.

In Fig. 4 we plotted our computed electronic and phonon DOS of Cu, both at room temperature and with cold and hot core-hole states. This comparison reveals that the DOS change considerably. In the case of the electronic DOS [Fig. 4(a)], each of which we plotted with reference to its own Fermi level, the presence of a core hole shifts the d band towards lower energies, while its width becomes significantly smaller, implicating that the $3d$ states of Cu become more localized, when a core hole is excited [15].

In many materials, when electrons are excited, the average bonding force is weakened and the solid cannot maintain its crystal structure [24,25]. In contrast, Mazevet *et al.* [26] experimentally observed a superheated state of ordered, electronically stabilized warm dense gold and also found that its melting temperature increases in the laser-excited state [27]. From our work we realized that the average AFCs of Cu and Ag become stronger both in the cold and in hot core-hole-excited state compared to the ground state. Figure 2 shows that the lattice remains stable even at $T_e = 30\,000$ K. In general, the variation of the effective interatomic potential should change the mechanical stability of the lattice, but in the case of noble metals we found no indication of any phonon mode instability both in the presence of core holes alone and with core holes and hot electrons. So it is clear that nonthermal melting cannot be the pathway for the relaxation of warm dense Cu and Ag. Instead, the laser-excited hardening of the phonon modes in warm dense noble metals leads to conclude that these systems relax thermally into a plasma state.

For the description of the plasma properties of WDM, the presence of an ordered crystal lattice should be taken into account. We can expect that the crystal structure will have an influence on the plasma properties that are related to the highly excited lattice vibrations. In the case of WDM with a highly ordered crystal, the relaxation is a faster process than in

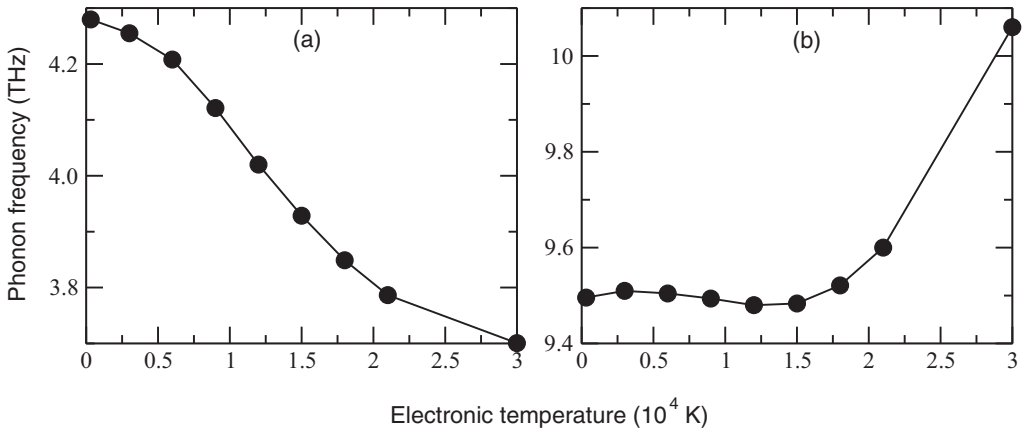

FIG. 3. Transverse (a) and longitudinal (b) acoustic phonon mode frequencies of Cu at the L point in the BZ with one core hole per atom as a function of the electronic temperature.

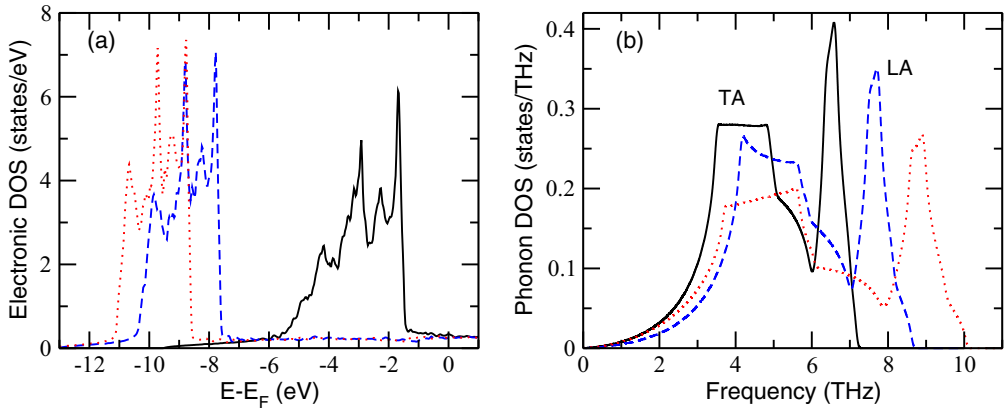

FIG. 4. (Color online) Electronic (a) and phonon (b) densities of states of Cu at room temperature (black solid), in the presence of cold (blue dashed) and hot, $T_e = 30\,000$ K (red dotted) electrons with one core hole per atom.

the gaseous plasma [28]. The experiments performed on warm dense silicon [29] and aluminum [30] samples suggest a very low electron-phonon coupling time. The electronic excitation of silicon weakens the covalent bonding, softens the lattice, and results in an electronically driven disordered lattice [27]. Such a laser-induced instability induces ultrafast nonthermal melting in silicon [19]. In the case of nearly free-electron metals like aluminum, the lattice stability appears to be mostly unaffected by the electronic excitation [27] and such solids show thermal melting on the picosecond time scale after the excitation [31]. In contrast, it is observed that in warm dense copper, which was created without a core hole in Ref. [18], the energy exchange rate between electrons and lattice vibrations is about 3 to 6 times faster [18] than the theoretically computed electron-phonon coupling constant [32]. In analogy to the above-mentioned finding, that the electron-lattice relaxation is more efficient in the solid than in the plasma phase [28], we suggest that the excess stability of the lattice attained in Cu and Ag at higher T_e due to an XUV or laser excitation may be responsible for the fast energy exchange rate in warm dense noble metals.

In conclusion, we have theoretically studied a transient, exotic state of highly ionized crystalline noble metals Cu and Ag. We observed how the electronic and phonon DOS as well as the phonon dispersion spectra are changed in core-hole states, with both cold and hot electrons. We found that the change in the AFC of the first nearest neighbors due to the presence of core holes and hot electrons cause the hardening of the potential energy surface. As a result the system gains extra stability.

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