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Energy transfer between electrons and ions in dense displacement cascades

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A theory of the energy exchange between valence electrons and ions in the dense displacement cascades in metals is proposed. It is shown that the theory based on the relaxation of the nonequilibrium electron-ion system gives a common basis for the electronic stopping power of slow ions due to valence electrons and for the energy transfer via an electron-phonon interaction. It is found that the energy loss owing to the electron-phonon interaction bears a close relationship to the electronic stopping power, but it is greatly enhanced because of the emergence of phonon excitations and band structure. The corresponding cooling rates of the thermalizing cascade are several times greater in metals with a strong electron-ion interaction than in metals with a weak interaction. A similar conclusion holds in the intermediate region, where the ions in the thermalizing cascade are essentially free to move but band-structure effects persist. However, conduction electrons play a role in the cooling of the cascade only if the dynamics of the ions gives rise to phonons.

I. INTRODUCTION

The passage of an energetic ion through a metallic medium leaves behind a displacement cascade, which rather soon attains local equilibrium and enters into the so-called thermal-spike stage.[1] Heat is dissipated out from the impact region mainly via molecular encounters and the duration of the thermal-spike phase of the cascade is rather long, of the order of tens of picoseconds. However, part of the energy is always transferred to the subsystem of valence electrons, which is capable of transporting heat much more efficiently than the ionic system. Whether or not valence electrons play a role in the heat dissipation process, depends of course on the rate of the energy transfer to them. Usually it is assumed, that for slow ions the only effect of the valence electrons is to provide a viscous background, which degrades the motion of secondary recoils.[2] In this case the energy loss can be calculated as a linear response of the homogeneous electron gas to the slowly moving massive ion. The resulting transfer is negligible for ions in a thermalizing cascade with the average energy at most a few eV per ion. If, however, the energy exchange occurs via the electron-phonon interaction, as proposed recently, electrons can take up a substantial amount of energy from the thermal spike and rapid quenching of the spike is possible in metals with strong electron-phonon coupling.[3,4]

The subject of electron-ion interaction in thermal spikes has remained controversial, because it is not amenable to direct experimental observation, and the theoretical approaches have not yet been able to state the conditions that are necessary for emergence of the electron-phonon interaction in thermal spikes. Furthermore, it is questionable whether phonons can exist in thermal spikes, which are supposed to be locally liquidlike regions.[5]

The electronic stopping power due to valence electrons and the electron-phonon interaction approaches seem to have little if any in common. The stopping theory of slow ions in electron gas[6,7] is not readily adapted to describe the energy loss of ions in the thermal spikes because it is derived for a single ion, whose movement is not correlated with the motion of other ions in the cascade. In thermal spikes this assumption cannot be taken for granted and the possibility of correlated motion must be taken into account. Similarly, the band-structure effects can be omitted in the electronic stopping power theories, but not in the energy-loss theory for thermal spikes. Furthermore, in the theories of the electronic stopping power, it is implicitly assumed that changes in the path of the projectile are small during several electron-ion encounters. In the thermal spike the velocities of the ions change at random all the time and the proper measure for the ion's energy is not the instantaneous kinetic energy but rather the average thermal energy. These notions suggest that the energy-transfer process should be described rather from the point of view of the relaxation of the nonequilibrium electron-ion system than from the point of view of the linear response of the homogeneous electron gas to the moving ion.

A similar approach was used recently to calculate the energy-transfer rate due to the interaction of electrons with dynamic excitations of the ions in the thermal spike.[8] Discussion in Ref. 8 was based on a specific model for excitations of ions, and many details were left open, as will be seen later on. In particular the connection of such a formulation with the more familiar theories of electronic stopping power were not considered. The electron-ion interaction in thermal spikes has been considered previously also by Caro and Victoria,[9] who pointed out the interrelation of the stopping power and the electron-phonon interaction regions in a semiempirical way. The motivation of this paper parallels to that in Ref. 9, with the difference that the present study is restricted solely to the role of valence electrons during the thermalization stage. We show that a theory based on the relaxation of the nonequilibrium electron-ion system can give a common theoretical basis for the electronic

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stopping due to valence electrons and for the energy loss caused by electron-phonon interaction in thermal spikes. Such a formulation elucidates the inherent similarities of these two phenomena and displays how they are the opposite limits of the same basic governing equation.

This paper focuses on formal derivations and results. The main emphasis is laid on the demonstration of how various energy-loss phenomena, owing to the presence of valence electrons, are interrelated. We have not made an attempt to prove or disprove the existence of electron-phonon interaction in thermal spikes, because it is clearly beyond the scope of the present study. Rather, we have only pointed out the basic physical assumptions needed to justify particular expressions for energy-transfer rates. The results are formulated so that contact is made with the previous results in the literature. Finally, model equations for the spike cooling are studied in order to assess the role of the energy transfer to conduction electrons in the cooling process.

II. MICROSCOPIC PROBABILITY OF ENERGY EXCHANGE

The basic task is to calculate the microscopic probability for the transfer of energy and momentum in collisions between ion and valence electrons due to electron-ion collisions. The energy exchange of ions and valence electrons occurs when an electron in momentum state $\mathbf{p}=\hbar\mathbf{k}$ with energy $\epsilon_{\mathbf{k}}$ scatters into a state $\mathbf{p}'=\hbar\mathbf{k}$ with energy $\epsilon_{\mathbf{k}'}$. In this scattering the momentum and energy of the electron are changed by an amount $\hbar\mathbf{q}$ and $\hbar\omega=\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'}$, respectively, (in the following the vector notation is retained only if necessary). Actually the ion is moving with velocity $\mathbf{v}$ with respect to the background electron gas, but the calculations can be carried out equally well in the frame of reference of the ions. Then the probability $w(\mathbf{q},\omega)$ for the momentum and energy transfer to conduction electrons can be written down in the level of a Born approximation as[10–12]

$$w(\mathbf{q},\omega)=\frac{2\pi}{N^2\hbar^2}\sum_{\mathbf{p},\mathbf{p}'}\delta_{\mathbf{p}-\mathbf{p}',\hbar\mathbf{q}}\,\delta\left[\frac{\epsilon_k-\epsilon_{k'}}{\hbar}-\omega\right]|v_{\mathbf{k},\mathbf{k}'}|^2S(q,\omega)\times\left[f(\mathbf{p}+\mathbf{p}_0)(1-f(\mathbf{p}'+\mathbf{p}_0))-\frac{n(\omega,T_L)}{1+n(\omega,T_L)}f(\mathbf{p}'+\mathbf{p}_0)(1-f(\mathbf{p}+\mathbf{p}_0))\right], \tag{1}$$

where $v_{\mathbf{k},\mathbf{k}'}$ is the spin independent local potential for the electron-ion scattering and it is normalized to the unit cell in a monovalent metal with N atoms. Electrons are described by the Fermi distribution $f(\mathbf{p}+\mathbf{p}_0)$, where $\mathbf{p}_0=m\mathbf{v}$ is the momentum of electrons due to the relative motion of ionic and electronic systems. The function $S(q,\omega)$ is the probability for the creation of the ionic density fluctuation with momentum $\hbar q$ and energy $\hbar\omega$. Different temperatures T_e and T_L are assigned to electron and ion distributions, respectively, to describe approximately the nonequilibrium distributions. Behind this so-called local equilibrium approximation is the assumption that electron-electron and ion-ion collisions are active to keep the distributions $f(\mathbf{p})$ and $S(q,\omega)$ in local equilibrium. The energy exchange depends on the inequality of the creation and the absorption of density fluctuations and therefore it is essential, even at high temperatures, to fulfill the condition of detailed balance $S(-q,-\omega)=S(q,\omega)n(\omega,T_L)/[1+n(\omega,T_L)]$.[10] The condition of detailed balance gives rise to the factor containing Bose-Einstein distributions $n(\omega,T_L)$.

We are interested in the velocity region $|\mathbf{v}|\ll v_F$, where v_F is the Fermi velocity of the electrons, so we can make the expansion $f(\mathbf{p}+\mathbf{p}_0)\approx f(\mathbf{p})+\mathbf{p}_0\cdot\nabla_{\mathbf{p}}f(\mathbf{p})$. Using the relation $\nabla_{\mathbf{p}}f(\mathbf{p})=-(\mathbf{p}/mk_BT_e)f(\mathbf{p})[1-f(\mathbf{p})]$ (in the following we will change in the Fermi distributions arguments from momentum to energy) and by noting the equality $f(\epsilon_p\pm\hbar\omega)[1-f(\epsilon_p)]=n(\omega,T_e)[f(\epsilon_p)-f(\epsilon_p\pm\hbar\omega)]$ the leading terms of Eq. (1) are obtained,

$$w(\mathbf{q},\omega)=\frac{2\pi}{N^2\hbar^2}\sum_{\mathbf{p},\mathbf{p}'}\delta_{\mathbf{p}-\mathbf{p}',\hbar\mathbf{q}}\,\delta\left[\frac{\epsilon_k-\epsilon_{k'}}{\hbar}-\omega\right]|v_{\mathbf{k},\mathbf{k}'}|^2S(q,\omega)\left[\frac{n(T_L)-n(T_e)}{1+n(T_L)}-\frac{\hbar\mathbf{q}\cdot\mathbf{v}}{k_BT_e}n(T_e)\right][f(\epsilon_p)-f(\epsilon_p-\hbar\omega)]\,. \tag{2}$$

Below Fermi temperatures $T_F\approx(5-10)\times10^4$ K we can assume a sharp Fermi surface and approximate

$$f(\epsilon_p)-f(\epsilon_p-\hbar\omega)\approx\hbar\omega\delta(\epsilon_p-E_F)\,,$$

where E_F is the Fermi energy. The matrix element $|v_{\mathbf{k},\mathbf{k}'}|$ of the interaction potential depends only on the difference $q=|\mathbf{k}-\mathbf{k}'|$. Because scattering occurs near the Fermi surface it can be evaluated for initial and final states lying at the Fermi surface. Then, after completing the first step of approximations we can ignore $\hbar\omega$ in the δ function in the resulting expressions (for validity of this approximation, see Ref. 13). Passing then into the high-temperature limit $T\gg\Theta_D$, where Θ_D is the Debye temperature, we can approximate $n(\omega,T)\approx k_BT/\hbar\omega$ to obtain,

$$w(\mathbf{q},\omega)=\frac{2\pi}{N^2}\sum_{\mathbf{k},\mathbf{k}'}\delta_{\mathbf{k}-\mathbf{k}',\mathbf{q}}|v_{\mathbf{k},\mathbf{k}'}|^2\delta(\epsilon_{k'}-E_F)\delta(\epsilon_k-E_F)\times S(q,\omega)[\mathbf{v}\cdot\mathbf{q}+\omega(1-T_e/T_L)]\,. \tag{3}$$

We have now an expression for the momentum and energy transfer, where all information of the ionic dynamics is contained in the dynamic structure factor. It will be seen in the following, how the present theory reproduces the electronic stopping power due to valence electrons and energy transfer due to the electron-phonon interaction, and how the form of $S(q,\omega)$ is of immense importance in determining the total rate of energy transfer.

III. ELECTRONIC STOPPING POWER REGION

The gas of valence electrons degrades the motion of slow ions by the effect of momentum loss in electron-ion collisions. The force $\langle \mathbf{F} \rangle$, which appears to brake the ion and thus degrade the relative velocity $\mathbf{v}$ of ion and electron gas, is

$$\langle \mathbf{F} \rangle = \sum_{\mathbf{q}} \hbar \mathbf{q} \left[\int d\omega \, w(\mathbf{q},\omega) \right] . \tag{4}$$

The resulting energy-loss rate (per one atom) of the ionic system is

$$\dot{U}_s = \langle \mathbf{F} \rangle \cdot \mathbf{v} . \tag{5}$$

Using Eq. (3) to evaluate $\dot{U}_s$, we note that due to the first term in the square brackets in Eq. (3), the sum rule

$$\int d\omega \, S(q,\omega) = S(q) \tag{6}$$

enters in the resulting expression. In the electronic stopping power region there are no static correlations between the positions of the moving particle and surrounding particles, so we can set $S(q) \approx 1$ in the following calculations. The resulting term in $\dot{U}_s$ is proportional to $q^2 |v_q|^2$. The second term in the square brackets in Eq. (3) gives a vanishing contribution, because the odd frequency moments of uncorrelated particles are zero.[14] The disappearance of this term is the manifestation of the physically self-evident fact, that thermal bath cannot transfer energy to a certain specific direction of the particle and so systematically speed it up.

In the surviving term it is taken into account that scattering occurs near Fermi surface, so that $q^2 = 2k_F^2(1-\cos\Theta_{\mathbf{k},\mathbf{k}})$. Transforming the double sum into an integral over wave-vector space by standard methods[13] and averaging $(\mathbf{v}\cdot\mathbf{q})^2$ over all directions of $\mathbf{q}$ and taking into account that the δ functions restrict the integrations over the Fermi surface S_F we obtain,

$$\dot{U}_s = \frac{2}{3}(\hbar k_F)^2 N(E_F) v^2 \left[\frac{2\pi}{\hbar} N(E_F) \int_{S_F} \frac{d\Omega_{\mathbf{k}}}{4\pi} \int_{S_F} \frac{d\Omega_{\mathbf{k}'}}{4\pi} (1-\cos\Theta_{\mathbf{k},\mathbf{k}'}) |v_{\mathbf{k},\mathbf{k}'}|^2 \right] , \tag{7}$$

where $\Omega_{\mathbf{k}}$ is the solid angle of wave-vector space and $\Theta_{\mathbf{k},\mathbf{k}'}$ is the scattering angle. The electronic density of states per particle is $N(E_F)$. If the kinetic energy of the moving ion is more than a few electronvolts the band structure is smeared out from the viewpoint of an ion and the density of states is essentially as for free electrons. The term in the square brackets in Eq. (7) is

$$\tau_{ss}^{-1} = \frac{2\pi}{\hbar} N(E_F) \int_{S_F} \frac{d\Omega_{\mathbf{k}}}{4\pi} \int_{S_F} \frac{d\Omega_{\mathbf{k}'}}{4\pi} (1-\cos\Theta_{\mathbf{k},\mathbf{k}'}) |v_{\mathbf{k},\mathbf{k}'}|^2 , \tag{8}$$

and it is the standard single scattering approximation for the electron-ion collision time, also called as transport relaxation time.[13] It is evident that Eq. (7) can be written now in a more compact form

$$\dot{U}_s = 2\frac{m}{M} \tau_{ss}^{-1} E_{\mathrm{kin}} , \tag{9}$$

where $E_{\mathrm{kin}} = \frac{1}{2}Mv^2$ is the kinetic energy of the slowing down ion. As a by product we find that $\langle \mathbf{F} \rangle = m\mathbf{v}\tau_{ss}^{-1}$, which is in fact the impulse approximation for the momentum loss (see, e.g., the discussion about Drude theory of resistivity in Ref. 15).

The rate of the energy loss with the relaxation time in Eq. (8) is identical to the result derived by d'Agliano *et al.*[16] from the Boltzmann equation for a heavy ion slowing down in homogeneous electron gas. The connection with the well-known electronic stopping theory by Ferrell and Ritchie[6,7] is made explicit using the phase-shift representation of the spherically symmetric, nonoverlapping potentials for $|v_{\mathbf{k},\mathbf{k}'}|$. Then the above form of τ_{ss}^{-1} can be expressed as[16–18]

$$\tau_{ss}^{-1} = \frac{8}{3\pi} \frac{E_F}{\hbar} \sum_l (l+1)\sin^2(\delta_l - \delta_{l+1}) , \tag{10}$$

where δ_l is phase shift of the lth partial wave function. In principle, τ_{ss} can be calculated on the basis of Eq. (10) finding the phase shifts of the appropriate muffin-tin potential[17] or for the potential based on the density-function formalism.[7] However, because we are interested in only valence electrons, a good estimate for τ_{ss}^{-1} is the value obtained from the metallic resistivity at the melting point.[18,19]

The above derivation demonstrates that starting from the formalism devised for the relaxation of electron-ion nonequilibrium states in a dense metallic medium, we recover the usual result of electronic stopping power of slow ions in homogeneous electron gas of valence electrons. This happens in the limit, where both the band structure and the correlations of ionic positions vanish.

The energy loss of single ions was derived considering momentum dissipation only and we were able to perform the calculations assuming the electron-ion collisions to be elastic. Consequently we have not yet specified how the kinetic energy lost by the ions is actually transferred to the electronic system. This problem is analogous to the Joule heating of metallic conductors and can be discussed following the lead of Tremblay *et al.*[20] The rate of change of the nonequilibrium Fermi distribution due to the force $\langle \mathbf{F} \rangle = m\mathbf{v}\tau_{ss}^{-1}$ is in the level of the Boltzmann equation[20]

$$\frac{\partial f}{\partial t}+\langle \mathbf{F}\rangle\cdot\nabla_{\mathrm{p}}f=-\frac{f-\bar{f}}{\tau_{ss}}\ , \tag{11}$$

where $\bar{f}=\int d(\Omega_{\mathrm{p}}/4\pi)f$ is the directional average of the Fermi distribution. Expanding f into ascending powers of $\langle \mathbf{F}\rangle\cdot\nabla_{\mathrm{p}}$ as $f=f^{(0)}+\delta f^{(1)}+\delta f^{(2)}+\cdots$, where $f^{(0)}$ is the equilibrium distribution, and substituting the expansion in Eq. (11) it is found that[20]

$$\delta f^{(2)}=t\int\frac{d\Omega_{\mathrm{p}}}{4\pi}\tau_{ss}(\langle \mathbf{F}\rangle\cdot\nabla_{\mathrm{p}})^2 f^{(0)}\ . \tag{12}$$

This term gives rise to the energy gain, which occurs at a rate

$$\dot{E}_{\mathrm{el}}=2N(E_F)\int d\epsilon\frac{\partial}{\partial t}(\epsilon\delta f^{(2)})\ . \tag{13}$$

Performing the resulting integration for free-electron bands we obtain

$$\dot{E}_{\mathrm{el}}=2\frac{m}{M}\tau_{ss}^{-1}E_{\mathrm{kin}}\ . \tag{14}$$

This proves that the energy lost by the ions is indeed transferred to the electronic system and the total energy of the electron-ion system is conserved. Note that although the form of the distribution is changed by the effect of the collisions, it relaxes back to the equilibrium distribution in the timescale of electron-electron collisions. Therefore, the local equilibrium assumption is not invalidated.

IV. ENERGY LOSS DUE TO ELECTRON-ION INTERACTION

The energy loss of ions in the thermal spike is determined by the ionic dynamics in an environment with local temperature T_L, where ions move at random with average thermal energy $E_{\mathrm{ther}}=(3/2)k_BT_L$. In the thermal spike the movement of the ions is correlated and the band-structure effects are bound to emerge. For these reasons we must retain throughout the calculations those features of $S(q,\omega)$ and $N(E_F)$ that are pertinent for dense metallic medium.

The rate of the energy transfer due to thermal motion of the ions is obtained summing up all possible energy transfers $\hbar\omega$ in inelastic electron-ion collisions, giving

$$\dot{U}_l=\int d\omega\,\hbar\omega\left[\sum_{\mathbf{q}}w(\mathbf{q},\omega)\right]\ . \tag{15}$$

Now the first term in square brackets in Eq. (3) vanishes, because it is odd with respect to ω. This term vanishes also for the crystalline medium, where the first frequency moment, the Placzek sum rule[21] is proportional to q^2. The corresponding term in Eq. (15) is proportional to q^3 and it drops out in the summation over $\mathbf{q}$. The nonvanishing contribution can be calculated provided that we find expression for $S(q,\omega)$. This is rather difficult for liquid metals, where $S(q,\omega)$ has a rich structure and has furthermore a complicated temperature dependence.[22] Fortunately we need only the second frequency moment of the dynamic structure factor, as the inspection of Eq. (15) after the substitution of $w(\mathbf{q},\omega)$ reveals. Pure liquid metals with ionic mass M obey the classical sum rule

$$\int d\omega\,\omega^2 S(q,\omega)=\frac{k_BT_L}{M}q^2\ , \tag{16}$$

which can be derived by theoretical arguments and has been also verified experimentally.[14] Note that liquid metals fulfill always the classical sum rule irrespective of the fact that they can support damped propagating collective modes even with wave vectors comparable to the inverse of the interparticle separation.[14,23] Applying the sum rule in Eq. (16) and performing the calculations similarly as in the preceding section, the rate of the energy transfer is seen to be

$$\dot{U}_l=2\frac{m}{M}\tau_{ss}^{-1}\Gamma\left[1-\frac{T_e}{T_L}\right]E_{\mathrm{ther}}\ , \tag{17}$$

where $E_{\mathrm{ther}}=(3/2)k_BT_L$ is the thermal energy per atom in the cascade and τ_{ss}^{-1} is as defined in Eq. (8). In the above equation we have introduced the parameter $\Gamma=N(E_F)/N_{\mathrm{free}}(E_F)$, which is the ratio of the band density of states to the free-electron density of states $N_{\mathrm{free}}(E_F)$. This is due to the fact that now we must retain the band density of states (see Eq. 7) because we are interested in temperatures which are of the order 10^4 K or below it. At these temperatures the band structure and the density of states is rather similar as in solid metals.[24]

An interesting situation arises near the solidification point, when the medium may give rise to undamped propagating collective modes or phonons. In this case the dynamic structure factor can be written down in the one-phonon approximation[15]

$$S(q,\omega)=\tfrac{1}{2}S(q)[\delta(\omega-\omega_q)+\delta(\omega+\omega_q)]\ , \tag{18}$$

where $S(q)=(q^2/M\omega_q^2)k_BT_L$ is static structure factor, also in the one-phonon approximation. The Debye-Waller factor and multiphonon corrections are omitted, because these corrections are known to cancel each other.[13,21] The above expression is also valid for amorphous solids, because in the one-phonon approximation the excitation spectrums of ionic vibrations are sufficiently similar in amorphous and crystalline solids.[11] There are now two possibilities with which to proceed in order to calculate the energy-transfer rate U_p in the electron-phonon system.

The first, most evident method is to invoke a specific model for lattice vibrations in order to obtain the dispersion relation for ω_q. Near the solidification we can treat electrons and ions as a two component plasma and the sound mode may be thought to be arising from the plasmon excitations.[25] Then the dispersion relation of phonons is $\omega_q=c_sq$, where $c_s=v_F\sqrt{m/3M}$ is the Bohm-Staver velocity of sound. With this dispersion relation the one-phonon approximation in Eq. (18) gives

$$\dot{U}_p=2\frac{m}{M}\tau_{ss}^{-1}\Gamma S(2k_F)\frac{E_F}{k_BT_L}\left[1-\frac{T_e}{T_L}\right]E_{\mathrm{ther}}\ . \tag{19}$$

In the derivation we have taken into account that the double integral over wave-vector space is dominated by the contribution from $q=2k_F$, which allows us to take the static structure factor out of the resulting integral.[18] An alternative way is to use the Faber-Ziman relaxation time $\tau_{\rm FZ}$ instead of τ_{ss} as in Ref. [8], but Eq. (19) is more illuminating for our present purposes. For weak scattering metals $\tau_{ss}^{-1}S(2k_F)$ is approximately equivalent to $\tau_{\rm FZ}^{-1}$.[18] Furthermore, $\tau_{ss}^{-1}S(2k_F)/k_BT_L$ is temperature independent and can be thus determined from the resistivity at the liquid state.

The above equation displays clearly how $\dot{U}_p$ depends on the ionic structure and band structure of the solid. The dependence $\dot{U}_p$ on the band density of states comes via parameter Γ and correlations in ionic positions enter through the static structure factors $S(2k_F)$. In addition to this factor, $\dot{U}_p$ is larger than $\dot{U}_s$ and $\dot{U}_l$ by a factor of $E_F/k_BT_M\approx 50$, where T_M is the melting temperature. This difference can be understood to be a consequence of the difference between the classical thermal velocity of sound $v_s=\sqrt{k_BT_L/M}$ and the Bohm-Staver velocity of sound $c_s=v_F\sqrt{m/3M}$ in a metallic system.

An alternative way to calculate the energy transfer due to the electron-phonon interaction is to use again the one-phonon approximation for $S(q,\omega)$ in Eq. (1) and approach the problem via the spectral function $\alpha^2F(\omega)$ for electron-phonon interaction. Substituting $S(q,\omega)$ from Eq. (18) into Eq. (3), one obtains after the integration of Eq. (15)

$$\dot{U}_p=4\pi N(E_F)\int d\omega\,\alpha^2F(\omega)(\hbar\omega)^2[n(T_L)-n(T_e)]\ , \tag{20}$$

where the spectral function $\alpha^2F(\omega)$ (Eliashberg function) is defined as[26]

$$\alpha^2F(\omega)=[\hbar N^2N(E_F)]^{-1}\sum_{\mathbf{k},\mathbf{k}'}|M_{\mathbf{k},\mathbf{k}'}|^2\delta(\omega-\omega_q)\delta(\epsilon_k-E_F)\delta(\epsilon_{k'}-E_F)\ . \tag{21}$$

We have used the standard definition (see, e.g., Ref. 13) of the coupling function

$$|M_{\mathbf{k},\mathbf{k}'}|^2=(\hbar q^2/2M\omega_q)|v_{\mathbf{k},\mathbf{k}'}|^2$$

in order to make connection with the results derived by Allen for the nonequilibrium electron-phonon system in a crystalline medium.[26] At high temperatures $T_L\gg\Theta_D$ the above equation can be simplified making the Taylor expansion to obtain,

$$\dot{U}_p=2\pi\hbar\eta N(E_F)\frac{k_BT_L}{M}\left[1-\frac{T_e}{T_L}\right]\ , \tag{22}$$

where

$$\eta=2M\int\omega\alpha^2F(\omega)d\omega \tag{23}$$

is the McMillan-Hopfield parameter, an average measure for the strength of the electron-phonon coupling.[13]

The advantage of this approach is that wealth of information of the function $\alpha^2F(\omega)$ or its moments is available, because many measurements can be used to probe them.[13,27] Furthermore, the McMillan-Hopfield parameter is rather insensitive to the specific form of the lattice vibration spectrum.[13,28,30] For transition and noble metals several estimates exist of McMillan-Hopfield parameter or the mass enhancement parameter λ related to η via relation $\eta=3\lambda M\Theta_D^2(k_B/\hbar)^2$, where Θ_D is the Debye temperature.[13] In general η varies between 0.5–7 eV/Å^2 and λ between 0.1–0.6 for transition metals (Refs. 26, 27, 29, 30 and 31). Some representative values are given in Table I.

The magnitude of energy transfer $\dot{U}_p$ calculated from Eq. (22) is comparable to the value obtained from Eq. (19). In both cases it is evident, that the phonon system provides much faster cooling rates of thermal spikes than the ensemble of independent classical particles. Similarly, in both expressions the dependence on the electronic density of states is explicitly displayed. The result in Eq. (22) is already known from Ref. 26, and even the results in Eqs. (17) and (19) could have been obtained from Eq. (9) by qualitative arguments. The main conclusion that stopping power due to valence electrons is much smaller than the energy transfer due to electron-phonon interaction is definitely not an unexpected one. However, these results are now derived from the common theoretical starting point, and the inherent similarity of the electronic stopping power with the energy loss due to the electron-phonon interaction is thus clarified. It is seen how the emergence of band-structure effects and the correlations of the ionic positions enhance the energy-transfer rates, and how ultimately in the solidification the appearance of phonons leads to energy-transfer rates, which are typical to crystalline metals. The crucial point that makes the difference between the solids with phonon-excitations and between the liquids with no phonons is the dynamic structure factor $S(q,\omega)$ and its sum rules. However, the final answer to the question, whether or not phonons exist in thermal spikes, is beyond the scope of the present study, and detailed molecular-dynamics studies are needed to give a definite answer.

The entrance of the system into the region of electron-phonon interaction is probably an abrupt one, reflecting the abrupt change in ionic dynamics. In particular, the possibility of continuous change is ruled out because the sum rule in Eq. (16) is obeyed always except at the solidification.[23] Only for extremely long wavelengths in the hydrodynamic region, the possibility of continuous change of $S(q,\omega)$ can take place,[14] but this region is of no interest in ion-solid interactions.

In order to link the electron-phonon interaction at low energies to the electronic stopping power at high energies, a smooth interpolation in terms of electron density was introduced by Caro and Victoria.[9] Their interpolation was done on empirical grounds and the criterion was a best fit to the theoretical predictions over various elec-

TABLE I. The temperature relaxation time τ_L of the ionic system. The McMillan-Hopfield and mass enhancement parameters η and λ, respectively, used in the calculations are given. The upper limit of the ratio Γ is from the density of electronic states, the lower limit is from the reduced resistivity from Ref. 46. The relaxation time τ is τ_{ss} for Ni, Pd, and Pt and τ_{FZ} for Cu, Ag, and Pt. The values corresponding to the upper- and lower-limit estimates of Γ are shown.

	Ni	Cu	Pd	Ag	Pt	Au
η (eV/Å^2)	3.8	0.9	3.5	0.5	6.7	0.9
λ	0.4	0.14	0.4	0.1	0.6	0.14
Γ	6–15	1	11–17	1	9–12	1
E_F (eV)	7.0	7.0	5.5	5.5	5.5	5.5
τ (fs)	0.1–0.3	2.1	0.2–0.3	3.5	0.15–0.2	1.3
$\tau_L{}^{a}$ (ps)	0.4–0.8	24	0.5–0.8	56	0.7–0.9	64
$\tau_L{}^{b}$ (ps)	0.5–1.3	10	1.4–2.2	39	2.1–2.9	38
$\tau_L{}^{c}$ (ns)	0.4	0.6	0.8	2.0	0.8	1.8

[a] From the McMillan-Hopfield parameter, see Eq. (22).

[b] From the Bohm-Staver speed of sound, see Eq. (19).

[c] Stopping power region, see Eq. (9).

tron density. The present discussion fulfills a minor gap intently left open in Ref. 9 providing a mechanism and a criterion for the crossover to the region, where the energy loss is dominated by the electron-phonon coupling. The omission of the possibility that the crossover to the electron-phonon dominated region may be abrupt and structure dependent was, of course, well motivated. The region, where only valence electrons are of interest and where electron-phonon coupling sets is only a minor and extreme part of stopping power region. The details of the crossover are of importance only in the late thermalization stage of the cascade. However, then the existence of the crossover may profoundly affect the cooling of the thermal spike.

V. COOLING OF THE THERMAL SPIKE

The role of the conduction electrons in the cooling of the thermal spike revolves around two questions. Does the energy transfer to valence electrons have any marked effect on the cooling of a typical thermal spike, and do the electrons act as a perfect heat sink? These problems are of relevance also for the computer simulations of the thermalization of the displacement cascades, where it is essential to know how the electron-ion interaction should be modeled.[9] In this section we try to give an answer to these questions within the framework of the simple thermal-spike model, which is generalized to take into account the energy transfer between valence electrons and ions.[32]

In the thermal-spike model[1,33] the energy of the projectile is shared by the ions in the neighborhood of its track. The line density F_D of energy (deposited energy) transferred to the lattice by the projectile defines the initial conditions for the thermal spike and acts as an instantaneous line source of heat for lattice atoms. The temperature distributions T_L and T_e of the ionic and the electronic subsystems evolve according to coupled heat diffusion equations

$$\frac{\partial T_L}{\partial t}=\alpha_L\nabla^2 T_L-\dot{U}/C_L \tag{24}$$

$$\frac{\partial T_e}{\partial t}=\alpha_e\nabla^2 T_e+\dot{U}/C_e\ , \tag{25}$$

where the high-temperature heat capacity for classical particles is $C_L=3k_B/2$ and for electrons $C_e=(2/3)\pi^2k_B^2N(E_F)T_e$ are used. The transport coefficients α_e and α_L are the bulk metallic and lattice heat diffusivities, respectively, and they are related to the respective heat conductivities through relation $\alpha_{e,L}=\kappa_{e,L}/C_{e,L}$. The electronic heat conductivity at $T_e>\Theta_D$ is $\kappa_e=\frac{1}{3}C_e v_F^2\tau_{\mathrm{FZ}}$ and it does not depend on temperature, because $\tau_{\mathrm{FZ}}\propto 1/T_e$. The heat conductivity κ_L of the ionic system is more complicated, but we ignore its temperature dependence in favor of simple analytical estimates.

Assuming that conduction electrons act as a perfect heat sink we can approximate $(1-T_e/T_L)\approx 1$ in the formulas for $\dot{U}$. The justification of this assumption within the framework of adopted two temperature model is discussed in detail later on. In this case the solution of Eq. (24) (in cylindrical coordinates) for the lattice temperature T_L is,

$$T_L(\rho,t)=\left[\frac{F_D/C_L}{4\pi\alpha_L t}\exp(-\rho^2/4\alpha_L t)\right]\exp(-t/\tau_L)\ , \tag{26}$$

where $\tau_L=[\dot{U}/C_L]^{-1}$ is the temperature-independent relaxation time for the lattice temperature T_L.

In order to obtain estimates for the relaxation time τ_L, we must first estimate the transport relaxation time τ_{ss}. As was pointed out in the preceding sections, the transport relaxation time can be obtained from the measured resistivity of the liquid metal. In the case of strong scattering transition metals the phase-shift calculations for τ_{ss} agree with the relaxation times obtained from the liquid state resistivity $\rho = m/ne^2\tau$.[18] In the case of weak scattering metals, τ corresponds to the Faber-Ziman relaxation time τ_{FZ}, which is approximately equal to $\tau_{ss}/S(2k_F)$.[34] It may be argued that for transition metals the effective number density of conduction electrons should be used throughout the calculations. Similarly there is some ambiguity as to what is the effective density of states of electrons at the Fermi surface. Bounds for the various estimates for τ_{ss} and τ_{FZ} are given in Table I with the corresponding estimates for τ_L.

The typical thermal spike, which is of interest in the ion-beam physics and radiation effects, is created by a track of the high-energy ion with initial energy density of order $F_D \approx 100-300$ eV/Å. The spike with such an energy content cools down to the solidification temperature in few tens of picoseconds, if only the ionic heat conduction is active. From the values of τ_L given in Table I, it is immediately seen that then only the energy transfer via phonons is capable to alter the cooling times of the thermal spikes. Furthermore, only in the strong scattering transition metals does the heat exchange seem to be rapid enough to provide marked shortening in quenching times of the thermal spikes.

However, just this possibility, although not supported by any compelling theoretical evidence, has revived the interest towards electron-ion interaction in displacement cascades.[35] The experimental findings show that ion-beam mixing is in noble metals Cu, Ag, and Au 4–10 times greater than in their high-resistivity counterparts Ni, Pd, and Pt.[36,37] Similar trends are also observed in the nonlinear sputtering[38,39] and in the particle bombardment induced vacancy loop production.[40] All these phenomena are related to the lifetime of the thermal spikes. It has been shown by detailed model calculations that the rapid quenching, which results from the electron-phonon interaction, may explain why strong coupling Ni produce 3–5 times less vacancy loops than weak coupling Cu.[4] Similarly, the model calculations for ion-beam mixing can be brought into good agreement with the experimental observations provided that energy transfer is due to the electron-phonon interaction, described by either Eq. (19) or Eq. (22).[32,41] These notions support the idea that spikes really quench much more rapidly in strong scattering metals than in the weak scattering metals. Nevertheless, final vindication is yet lacking and the above-mentioned models are only tentative, until more conclusive evidence, e.g., from computer simulations exist to support the idea of phonon modes in thermal spikes.

We conclude this section estimating the upper limit for the rise in the electron temperature, in order to justify the assumption that electrons act as a perfect heat sink. Because lattice temperature distribution is much narrower than that of the electrons it is, from the point of view of electrons, a line source of heat. It is readily shown from Eq. (26) that this source has a strength

$$S(t) = (F_D/C_L)\tau_L^{-1}\exp(-t/\tau_L)\ . \tag{27}$$

Source $S(t)$ is now an upper limit estimate for the effect of the coupling term in Eq. (25), because in its derivation we have ignored the possible reduction of the energy-transfer rate due to the rise in electron temperature. The rise in electron temperature caused by the line source $S(t)$ is obtained by standard techniques,[42] giving

$$\Delta T_e(\rho,t) = \left[\frac{F_D/C_e}{2\pi\alpha_e t}\right]\int_\mu^\infty \zeta \exp[-\zeta(1-\mu^2/\beta^2)] \times \frac{\exp(-\beta^2)}{\beta}\,d\beta\ , \tag{28}$$

where we have introduced dimensionless variables $\zeta = t/\tau_L$ and $\mu = \rho/\sqrt{4\alpha_e t}$. In order to compare the electron and lattice temperatures, we average both of them at the cascade core $\rho < \sqrt{\alpha_L t}$. The ratio $\langle \Delta T_e \rangle / \langle T_L \rangle$ of the averages is

$$\frac{\langle \Delta T_e \rangle}{\langle T_L \rangle} \approx 8\frac{C_L}{C_e}\zeta \int_0^{\sqrt{\alpha_L/\alpha_e}} d\mu\,\mu \int_\mu \frac{\exp(-\beta^2)}{\beta}\,d\beta\ . \tag{29}$$

Expressing the above integral in terms of the exponential function E_1 Ref. (43) and using the fact that during the high-temperature stage (small times) $\zeta \leq 1$, we obtain an estimate

$$\frac{\langle \Delta T_e \rangle}{\langle T_L \rangle} \leq 8\frac{C_L}{C_e}\int_0^{\alpha_L/\alpha_e} \beta^{3/2}E_1(\beta)\,d\beta \leq 2\frac{C_L}{C_e}\left[\frac{\alpha_L}{\alpha_e}\right]^{5/2} \approx 2\left[\frac{\Gamma}{13}\right]^{3/2}\left[\frac{\kappa_{L,M}}{\kappa_e}\right]^{5/2}\left[\frac{T}{T_M}\right]^{11/4}\ , \tag{30}$$

where in the latter step the asymptotic expansion of E_1 was used, and for clarity heat conductivities are used instead of heat diffusivities. In order to obtain the upper limit for ΔT_e, we have now in Eq. (30) assumed that the ionic heat conductivity at temperatures above melting point can be approximated from the kinetic theory with the result $\kappa_L \approx \kappa_{L,M}\sqrt{T/T_M}$, where $\kappa_{L,M} \approx 1$ W/mK is the lattice heat conductivity at melting temperature.[44,45] Note that the electronic heat conductivity at high temperatures is temperature independent[46] and can be obtained from measured heat conductivities or via the Wiedemann-Franz law. For strong and weak scattering metals values 50 and 150 W/mK are typical ones, respectively.[47] With these values it is seen immediately, that even at temperature $T \approx 10^4$ K one obtains for strong scattering metals $\langle \Delta T_e \rangle / \langle T_L \rangle \approx 0.05$. For weak scattering metals the rise in electron temperature is completely negligible. Therefore, we may safely assume that within the reasonable bounds for the values of parameters appearing in Eq. (30), the rise in the electron temperature is at most 10% of the average lattice temperature at the spike core. Therefore, T_e/T_L in the coupling term $\dot{U}$ in Eqs. (24) and (25) can be set to zero without significant loss of accuracy even for strong coupling transition metals. Physically this means that, in practice, electrons act as a perfect heat sink in all metals.

The present conclusion that electrons are a perfect heat sink is in contradiction with the notion made in Ref. 3 that in strong coupling metals electrons are in equilibrium with the lattice for a substantial part of the spike's lifetime. The contradiction arises probably from the fact, that in Ref. 3 the two-temperature model was not used and then heat diffusivity α_e of the electronic system is proportional to $1/T_L$, whereas in the two-temperature model it depends on $1/T_e$. The dependence of α_e on the instantaneous lattice temperature causes the electrons to be trapped in the hot spike, which leads to anomalously high-electron temperatures and thus hinders the heat dissipation to electronic system. In our two-temperature model T_e rises gradually from the ambient temperature, because the rise due to energy gain is compensated by the cooling due to effective heat conduction. Both models have shortcomings owing to the fact that transport coefficient is well defined only in cases where electrons and phonons are in equilibrium. The two-temperature model is perhaps more self-consistent, and therefore favored in these kind of nonequilibrium situations.[48,49] Therefore, we emphasize, that the present conclusion holds within the validity of the adopted two-temperature model. It would be extremely useful to perform calculations based directly on the use of kinetic transport equations in order to judge which model is more realistic.

VI. DISCUSSION AND SUMMARY

We have studied the energy transfer between conduction electrons and ions in the thermalizing energetic displacement cascades in metals. A new theoretical formulation is given, which in the case of valence electrons extends the electronic stopping theory into the region, where electron-phonon interaction emerges. Most importantly, these different phenomena are shown to be consequences of the same basic rate equation, which governs the momentum and energy transfer in nonequilibrium electron-ion system. The present derivation clarifies also the role of ionic dynamics in the thermal spike and points out that the crucial information needed to assess the nature of the electron-ion interaction is contained in the dynamic structure factor for ions in the thermal spike.

In the stopping power region the energy exchange rates due to valence electrons derived here are similar to the previous results to be found in the literature. Similarly the energy exchange rate for the electron-phonon system has been derived a long time ago[50] and also recent improvements exist.[26,51] These results are basically similar to the energy transfer obtained considering the classical problem of the emission of sound waves by an electron moving through an elastic medium.[50,52] Also the heuristic approach based on electron diffusion in hot spike leads to a similar kind of energy transfer.[3,4] Therefore, in this respect, no new unexpected results are introduced; of interest here is only the way to obtain them.

From the present analysis we cannot judge whether or not electron-phonon interaction is operating in thermal spikes. However, the analysis shows that the energy exchange occurs either as in the system of uncorrelated ions or by electron-phonon interaction. The change between these two regions is probably an abrupt one. The energy loss due to stopping power is of no interest for the thermalizing cascade with ion energies below few electron volts. Only the energy transfer via electron-phonon coupling can significantly alter the cooling of the thermal spike.

Curiously, the experimental findings give indirect support to the belief that electron-phonon interaction is operating in thermal spikes. Unfortunately the support is obtained indirectly through agreement of model calculations of ion-beam mixing with measurements, and that cannot yet vindicate the idea of electron-phonon interaction operating in thermal spikes. The final judgment of the existence of electron-phonon interaction in thermal spikes is left therefore for the future. At least we know now that further studies should be focused on the dynamic structure factor of the ions.

In summary, the final expressions for the energy transfer reproduce the known results for electron-phonon interaction at low energies and links it with electronic stopping power due to valence electrons. The practical utility of the present results is limited to the late thermalization stage of the cascade, where only valence electrons participate in the energy dissipation process. The contribution we have given to the already existing extensive knowledge of these topics is the common theoretical starting point based on the relaxation of the nonequilibrium electron-ion system.

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